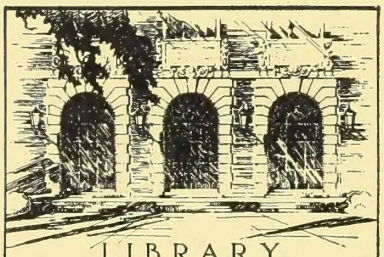

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MOLECULAR ADDITION COMPOUNDS OF SILVER WITH OLEFIN AND AROMATIC MOLECULES

Brad Wayland June 19, 1962

I. INTRODUCTION

The first studies of silver olefin complexes were concerned with the effects of alkyl substituents on the relative stabilities of the complexes. Alkyl substitution in the olefin molecule created opposing electronic and steric effects on the relative complexing ability of the olefin (1). The position of the alkyl group was found to be particularly important. Studies of a series of butene isomers demonstrates that the cis 2-butene complex is much more stable than that of the trans isomer (2). A similar study of pentene isomers showed that the complex of cis-2-pentene was more stable than that of the trans isomer (3).

Olefin	Agentation Constant K_1
1-butene	119.4
2-methyl propene	71.5
cis-2-butene	62.5
trans-2-butene	24.6

The effect of ring size and strain on complexation of Ag^+ has been studied for a series of unsaturated ring compounds (4)(5). The relative equilibrium constants are found to increase as the strain in the ring increases.

Olefin	Relative Equilibrium Constant K_1
cyclopentene	23.6
cycloheptene	4.2
cyclohexene	3.65

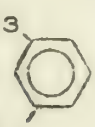
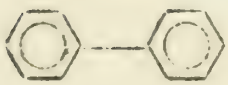
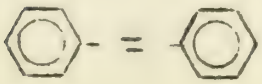
The effects of ring strain on an exocyclic double bond have also been studied (5). Formation constants of the methylenecycloalkanes show only a slight dependency on ring size.

Olefin	Relative Equilibrium Constant K_1
methylenecyclobutane	17.9
methylenecyclopentane	13.3
methylenecycloheptane	14.4
methylenecyclohexane	11.9

Silver aromatic complexes are also subject to both steric and electronic effects (6)(7). Thus the substitution of a methyl group

aromatic	argentation constant K_1
benzene	1.10
toluene	1.19
ethyl benzene	.98
t-butylbenzene	.90
o-xylene	1.43
m-xylene	1.35
p-xylene	1.14
m-diethylbenzene	1.06
m-diisopropylbenzen	.93
p-di t-butylbenzene	.62
1,2,3,4 tetramethylbenzene	1.69
1,2,4,5 tetramethylbenzene	.88

onto the benzene ring increases the basicity of the aromatic molecule and the argentation constant increases. However, as the steric requirem . of the alkyl group increase from methyl- to t-butyl- the argentation constant decreases. The position of the alkyl groups in the aromatic molecule also affects the formation of the addition compound with silver. Thus 1,2,3,4 tetramethylbenzene has a much larger agentation constant than 1,2,3,5 tetramethylbenzene. The energy of the highest occupied orbital in the aromatic is found by Fukui to be a good measure for complex formation. This indicates that the use of ionization potentials by Nakajima (9) to correlate the relative ease of complex formation is valid.

aromatic	K_1	relative delocal. energy	Energy of the highest occupied orbital
	2.41	1.333 β	-1.000
CH_3 	2.95	1.418 β	-.823
CH_3  CH_3	3.03	1.466 β	-.763
	3.08	1.600 β	-.618
	3.07	1.798 β	-.605
	3.94	1.370 β	-.705
	6.3	2.139 β	-.504

It is also recognized that polarizability is another factor which varies slightly for each aromatic molecule. Ion induced dipole interactions are not uniform from one aromatic molecule to the next. No correlation between polarizability and complex stability has yet been published, but a paper by Fukui is now being prepared (8).

II. STRUCTURE

The structures of silver olefin complexes are not well defined. It is generally assumed that the silver ion is symmetrically located above the plane of the olefin in the π cloud (10)(11). The suggested structure for the norbornadiene silver complexes places the silver ion in an exo configuration (12). This conforms with the model suggested by Winstein and Shatavsky for the electrophillic attack Br_2 on an olefin (13).

1:1 complex

1:2 complex

The structure of the silver aromatic complexes are better understood. An x-ray analysis of the silver benzene complex by Rundle showed that silver ions lie above and below the benzene ring over bonds one and four of each ring (14)(15). Thus silver benzene is an infinite polymer. A recent Raman spectra study has given similar results (16).

silver benzene complex

o carbon

O Ag^+

NO_3^- is excluded

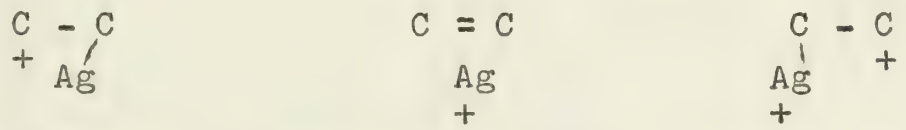
For the general case of any aromatic, Mulliken suggests that the silver ion will coordinate preferentially above and between two adjacent unsubstituted ring carbons when these positions are available (17). This model for the silver aromatic structure explains why there are significant stability differences between the complexes formed by ortho, meta and para xylene (6)(7).

The structure of silver cyclooctatetraene has been extensively studied by x-ray analysis (18-21). Silver ion is found to interact with two nonadjacent π bonds of the C_8H_8 molecule at Ag-C distances

of 2.46, 2.51, 2.78 and 2.84 Å. Somewhat longer Ag-C distances join the monomer unit into infinite chains along the c axis.

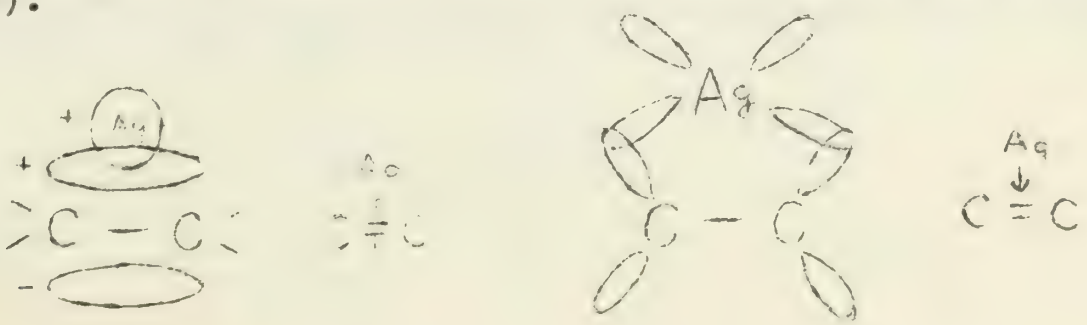
III. BONDING

The bonding in silver olefins was at first considered to be essentially the sharing of a pair of π electrons of the olefin with the Ag^+ (21)(23). This model was quickly discarded for free rotation would be allowed in the complexed olefin, and no rearrangement of cis and trans isomers was observed upon complexation (24). Winstein and Lucas suggested that the silver olefin bond involved three resonance forms (1).

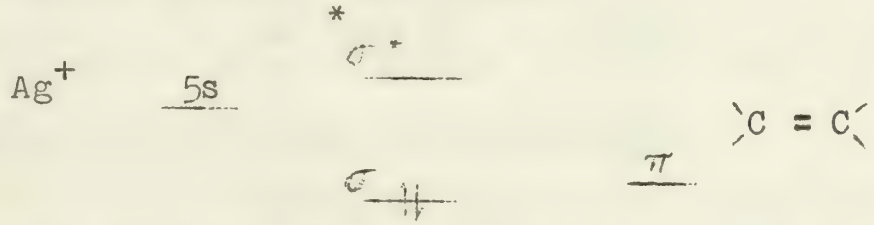


Similar metal to carbon σ-bonding has been proposed by Babushkin, Gribov and Hellman (25)(26). Recent N.M.R. and I.R. studies by Powell and Sheppard indicate that the olefin is changed only slightly upon complexation (27). In terms of the Winstein and Lucas model, the no bond structure $\left(\begin{array}{c} C = C \\ Ag \\ + \end{array}\right)$ must predominate.

A more satisfying model for the silver olefin bond was suggested by Dewar (10).



The vacant 5s orbital on silver ion is capable of overlapping the bonding π orbital on the olefin to form a σ bond. The filled 4d orbitals on the silver ion have the proper symmetry to overlap the vacant antibonding molecular orbitals of the olefin. The combination of the two oppositely directed bonds leaves the olefin with a much smaller positive charge than would be the case in a normal π complex. If the silver ion is situated in the center of the π cloud in the ethylene silver complex, then the complex has C_{2v} symmetry. The molecular orbitals formed by the overlap of the silver 5s orbital with the π bonding orbital of ethylene both have A_1 symmetry. The electric dipole operator in the z direction is also A_1. Therefore, charge transfer from the $\sigma \rightarrow \sigma^*$ is allowed. This suggests that the most probable position for the silver ion in the complex is directly above the carbon carbon double bond.



Traynham and Sehert contend that little or no σ bond character can be ascribed to the silver olefin complex since the complex is readily dissociated and no isomerization or polymerization of the olefin is observed (4). Traynham and Sehert suggest that it is adequate to describe the silver olefin complex as a π complex in which only the deformation of the π orbitals on the olefin is significant.

The bonding in silver aromatic complexes can be described in much the same manner as that for the silver olefin complexes, however, the highest filled π molecular orbital of benzene is not of the proper symmetry to give charge transfer if the silver ion is placed on the benzene six fold axis (28)(17). The highest filled π molecular orbital of benzene belongs to the irreducible representation e_1, while the lowest acceptor orbital of silver has A_1 symmetry. The silver ion moves to a position of lower symmetry where charge transfer becomes allowed. The empty e_2 π orbitals overlap the silver d orbitals which partially balances the charge transfer (29).

Rundle and Smith observed that the benzene molecule in the silver benzene complex is significantly distorted (14)(15). The carbon-carbon bond nearest to the silver ion becomes shorter. This distortion can only be explained as due to the polarization of the π electrons by silver increasing the electron density in the bonds nearest the positive silver ion. Thus polarization terms must also make a significant contribution to the total bonding.

Origin of Steric Effects

Cis olefins in general form much more stable complexes with silver than the trans isomer (2)(3). If the silver ion lies above the plane of the olefin in the π cloud, then steric effects should be small. Cis olefins, having two alkyl groups on one side of the molecule, are strained due to bond oppositions. The strain is partially relieved by a slight twisting about the double bond. The twisting about the double bond deforms the π orbital which, according to Gardner, facilitates polarization of the π electrons and thus stabilizes the complex (11). The effects of ring strain on cyclic olefins may be similarly explained. A. Cope reported that trans-cyclooctene preferentially reacts with silver and may be quantitatively separated from the cis isomer (30). This appears to be an anomolous result. However, a conformational analysis of cyclooctene shows that the trans isomer is more strained than the cis isomer. Thus the π electron cloud of the trans is more easily polarized and a stronger bond results

Applications of Silver Olefin Complexation

The stability differences between cis and trans olefin complexes with silver have been used by the organic chemist to separate geometrical isomers (30)(34). Silver ion has also been used as a means of trapping and stabilizing the short lived cyclobutadiene molecule(35). Complex formation may possibly be used as a means of trapping other short lived olefin intermediates in organic reactions.

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NUCLEOPHILIC DISPLACEMENTS ON PHOSPHORUS

G. D. Shier June 26, 1962

I. INTRODUCTION

The reactions of phosphorus compounds are interesting because of their analogy to carbon chemistry, their importance in living systems, and the availability of "d" orbitals for bonding. The existence of five coordinate phosphorus in PCl_5 and pentaphenyl phosphorus raises the possibility of metastable five coordinate intermediates in displacement reactions, and this possibility has been explored. This seminar will deal with some of the less complicated and more intensively studied reactions of phosphorus compounds and will try to interpret them in terms of kinetic and mechanistic parameters.

II. THE REACTIONS OF ACID FLUORIDES

The most thoroughly investigated class of compounds is the R_2POF series where R can be an alkyl, alkoxy, or amide group. Aksnes(1) has studied the effect of alkoxy versus alkyl substitution in the bimolecular alkaline hydrolysis reaction of R_2POF. His data are given in Table I. It is apparent that the activation energy increases and the rate decrease with the replacement of alkyl groups by alkoxy groups.

The inductive effect of oxygen in a sigma bond to phosphorus is more strongly electron withdrawing than for a bond between carbon and phosphorus, and this decreases the shielding of the phosphorus nuclear charge in the case of alkoxy substituents. However, as the phosphorus nucleus becomes less shielded, conjugation between the electron pairs on oxygen and the phosphorus atom becomes more favorable. On this basis a decrease in shielding of phosphorus will facilitate bond making and retard bond breaking. An increase in the conjugation effect will retard bond making, reducing the residual positive charge on phosphorus seen by an incoming nucleophile. The effect of conjugation on bond breaking will depend on the ability of the leaving group to strengthen its bond to phosphorus by conjugation. Implicit in this argument is the assumption of a five coordinate transition state.

Halmann(2) has investigated the hydrolysis of R_2POF where R is a methyl or isopropoxy group. He found no ^{18}O exchange for the phosphoryl group during the reaction, and general acid-base catalysis. The lack of ^{18}O oxygen exchange is interpreted as eliminating fast reversible addition of water in the transition state, but reversibility implies equivalence of the oxygen of the attacking group and of the phosphoryl group, which is questionable. Base catalysis may be due to greater rate of attack of hydroxide as compared to water, and acid catalysis may be due to protonation of the leaving group. Acid catalysis has not been observed where chloride is the leaving group, and hydrogen bonding is much less effective for chloride than for fluoride.

The effect of the calculated entropy of activation in Table I is to oppose the effect of the activation energy. Aksnes(3) has used the shift of the infrared stretching frequency of the phosphoryl group upon hydrogen bonding with phenol as a measure of the polarizability of the phosphorus compound. This work indicates that alkoxy groups enhance polarizability. On this basis the entropy effect can be explained by greater delocalization of charge in transition state and consequently greater desolvtion of the transition complex. Desolvation causes an increase in entropy giving a less negative overall entropy of activation. Steric effects often appear in entropy terms, and so it must be assumed that the steric effects of the ethyl and methoxy groups are similar.

Heath(4) has worked on the kinetics of alkaline hydrolysis of R_2POF compounds where R is a primary or secondary alkyl amido group. His data is neither good enough nor complete enough to separate the various steric, inductive, and conjugative factors, but it does indicate great steric hindrance for compounds where both R groups are secondary amido groups. Models are said to show these compounds to be very rigid.

The reactions of R_2POF compounds have been studied by other workers with varying results due to the complexity of the effects. The rates of reaction with oximes(5) and hydroxamic acids(6) have been found to correlate well with the basicities of the nucleophiles. Larsson has studied the alkaline hydrolysis of alkyl methylphosphonofluoridates(7), and the reaction of these compounds with hydrogen peroxide(8). Epstein etal. (9) have found that catechol reacts faster than phenol with alkyl methylphosphonofluoridates due to hydrogen bonding in the transition state.

III. THE REACTIONS OF ACID CHLORIDES

Dostrovsky and Halmann(10) studied the solvolysis, amminolysis, and reactions of anions with phosphorochloridates. For the reactions with anions they found the order $F^- > EtO^- > C_6H_5O^- > EtOH$, $C_6H_5S^-$, acetate. The reactivity of fluoride ion was about six times slower in 60% aqueous ethyl alcohol than in dry alcohol. This is possibly due to stronger hydrogen bonding between fluoride ion and water as compared to ethyl alcohol.

Amminolysis of diisopropyl phosphonochloridate with di-normalbutyl amine in several solvents showed a rather interesting behavior. The rate of the reaction increased smoothly with the increase in dielectric constant of the solvent for nonhydroxylic solvents, but the rate in ethanol with dielectric constant 26 was between benzene and dioxane with dielectric constant 2.3. This is especially interesting in view of the fact that almost all other work has been done in hydroxylic solvents.

Miller(12) has reacted O,O-diphenyl phosphorochloridothioate with a series of oxygen and sulfur nucleophiles and found that the plot of pK_a of the nucleophile versus the negative logarithm of the rate constant for ten nucleophiles gives a curved line with little scatter. The anions of benzophenone and acetone oximes are much more reactive than their basicities would indicate, and a specific mechanism has been proposed for them.

A thorough discussion of the hydrolysis of phosphonochloridates(13) has been given, the conclusions being similar to those for the phosphonofluoridates.

IV. OTHER DISPLACEMENT REACTIONS

Optically active o-ethyl ethylphosphonothioic acid has been isolated (14) and used to study the steriospecificity of displacements on phosphorus. Displacement reactions carried out using hydrogen sulfide, n-propyl mercaptide, and ethoxide ions in ethanolic solution indicated that inversion of configuration had taken place. A preliminary communication on other similar work has appeared (15).

The kinetics of alkaline hydrolysis of phosphonate esters has been studied(16) and found to proceed by SN2 attack of hydroxide on phosphorus. The rates of hydrolysis decrease smoothly with increasing size of the alkyl group, but the activation energy and preexponential factors show no regular pattern.

The reaction of optically active methylethylphenylbenzylphosphonium iodide with hydroxide and alkoxide ions has been studied (17, 18). The reaction with hydroxide gives optically pure methylethylphenylphosphine oxide. The authors say that the hydroxide ion can add reversibly to any face of the tetrahedron, and the conjugate base of any of the trigonal bipyramidal intermediates can be formed by reversible reaction with another hydroxide ion. Since the benzyl group forms the most stable anion, the only conjugate base that decomposes is the one where the oxygen atom and the benzyl group are colinear.

V. SUMMARY AND CONCLUSIONS

It has not been found necessary to postulate the existence of a stable five-coordinate intermediate in any of the displacement reactions on phosphorus that have been studied. The evidence favors a straight forward SN2 reaction mechanism where bond making and bond breaking influence the rate to varying degrees. Some authors(12) cite the strong rate dependence on the bacisity of the nucleophile as evidence for bond making as the rate determining step. This hypothesis has not been tested with a variety of leaving groups or in non hydroxylic solvents. The strong phosphorus fluorine bond probably accounts partially for the slower reactions

and higher activation energies of phosphorofluoridates as compared to phosphorochloridates. The existence of a rapid reversible equilibrium step preceeding displacement has not been demonstrated in any case, and it seems better to assume a straight forward nucleophilic attack. Steric effects on rate constants are analogous to those found in carbon chemistry.

Much work remains to be done in the area of organophosphorous mechanisms. In particular, it would seem desirable to know more about conjugative versus inductive effects, solvation effects, and the effect of variation of the leaving group.

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Table I

Compound	K(hydroxide)	E_A	S^I	I.R. Stretch(cm^{-1}) P=O	I.R. Stretch(cm^{-1}) P-F	Phenol Association at 20° in CCl_4
$(MeO)_2POF$	18.2	11.6	-16	1308	864	26.3
$(MeO)EtPOF$	49.1	10.1	-19	1295	858	82.5
Et_2POF	726	8.3	-20	1278	845	129.9

APPLICATIONS OF GROUP THEORY TO INORGANIC CHEMISTRY

Keith F. Purcell July 12, 1962

INTRODUCTION

Group theory can be applied quite easily to many problems in inorganic chemistry and through an understanding of a few basic principles, one may attain a great deal of insight into otherwise incomprehensible phenomena. It is the purpose of this seminar to demonstrate the success of group theory and the ease with which it may be applied to inorganic problems. The mathematical foundations of the theory will be taken for granted but they can be found in several texts (1,2,3,4,5).

STRUCTURE DETERMINATIONS

Many molecular structures have been ascertained or at least reduced to a few possibilities by application of group theory to the infrared and Raman spectra of the compounds. To illustrate the procedure of making a structure assignment, the investigations of Lord, et. al., (6) into the structure of IF_5 will be reviewed.

The first step in this process is to write down all the possible spatial arrangements of the atoms in the molecule. For each structure we determine the point group to which it belongs on the basis of whatever symmetry elements the configuration possesses. Finally, the number of infrared active and Raman active vibrational modes for each point group are determined. Through a comparison of the theoretical with the observed number of frequencies we can limit the number of possible structures or in some cases conclude the actual structure.

For IF_5 there are seven possible symmetries but only one will be discussed in detail. If the five fluorine atoms are arranged in a square based pyramid with the iodine atom at the center of the square, the point group which describes this structure is C_{4v}.

Utilizing the displacement coordinate approach, the motions of each atom are defined in terms of three vectors in the x,y, and z directions (displacement coordinates). The reducible representation generated by the displacement coordinates is found by performing each of the symmetry operations of the group on the molecule and noting which vectors are taken into themselves or their negatives. Each vector taken into itself contributes +1 to the character, into its negative, -1, and all others, 0. The sum (character) is then placed in the column of the symmetry operation.

The reducible representation is decomposed into the irreducible representations which it contains by means of the following equation,

$$n^{(\gamma)} = \frac{1}{h} \sum_j h_j \chi_j^{(\gamma)} \chi_j$$

h = number of operations in the group

h_j = number of operations in the jth set of operations

$\chi_j^{(\gamma)}$ = the character of the γth irreducible representation for the jth operation

χ_j = the character of the reducible representation for the jth operation

$n^{(\gamma)}$ = the number of times the γ the irreducible representation is contained in the reducible representation.

The normal modes of motion of the molecule are represented analytically by normal coordinates, one coordinate for each mode. It can be shown that each normal coordinate generates an irreducible representation of the point group. The symmetries of the normal modes of motion are finally arrived at by subtracting out the symmetries of the translational and rotational degrees of freedom. (See last page). As a final check, the final number of symmetry species should equal 3N-6 (for non-linear molecules).

$$\Gamma_{(motion)} = 4A_1 + A_2 + 2B_1 + B_2 + 5E$$
$$\Gamma_{(vib.)} = 3A_1 + 2B_1 + B_2 + 3E$$

Now that the symmetries of the normal modes are known, the optically active modes are determined from the fact that only those transitions are allowed for which the transition integral

$$\int \psi_n' |P| \psi_n \neq 0$$

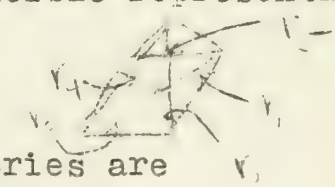
This is equivalent to saying that the direct product of the irreducible representations corresponding to each function in the integral must contain the totally symmetric irreducible representation of the point group.

Since the ground state vibrational symmetry of any molecule is the totally symmetric symmetry, only those modes whose symmetries are the same as any of the "T"s are infrared active. Those modes whose symmetries correspond to any of the "α"s are Raman active. In addition, any totally symmetric modes are Raman active and polarized. With these rules in mind we can compare the number of Raman lines, the number of infrared lines, polarized lines and coincident lines (total and polarized) found by experiment with the number predicted for each point group and eliminate unlikely symmetries. This analysis led Lord, et. al., to the conclusion that IF_5 possesses C_{4v} symmetry.

HYBRID ORBITAL FORMATION

Again we will use IF_5 as an example. To determine the iodine atomic orbitals which will combine to give hybrid orbitals of the proper symmetry, five labelled lines (representing sigma bonds) are drawn from the iodine atom to the fluorine atoms. These bonds are the basis for a reducible representation as before. (See last page.)

$$\Gamma_{(hybrid)} = 2A_1 + B_1 + E$$



Possible combinations with these symmetries are

sd^4	sdp^3
sd^2p^2	pd^4
spd^3	d^2p^3

Since the valence shell configuration for iodine is $5s^2 5p^5 5d^0$, we can predict that the combination of atomic functions with the lowest "hybridization energy" will be the correct one and, in this case, d^2p^3 is the most likely candidate. It is interesting to note that Kimball (7) predicted the symmetry of IF_5 to be C_{4v} on the basis of this method.

It is also interesting to note that, as one would anticipate, the d_{z^2} orbital is involved in the axial bond while the $d_{x^2-y^2}$ is involved in formation of the equatorial bonds.

MOLECULAR ORBITAL SCHEMES OF COMPLEXES

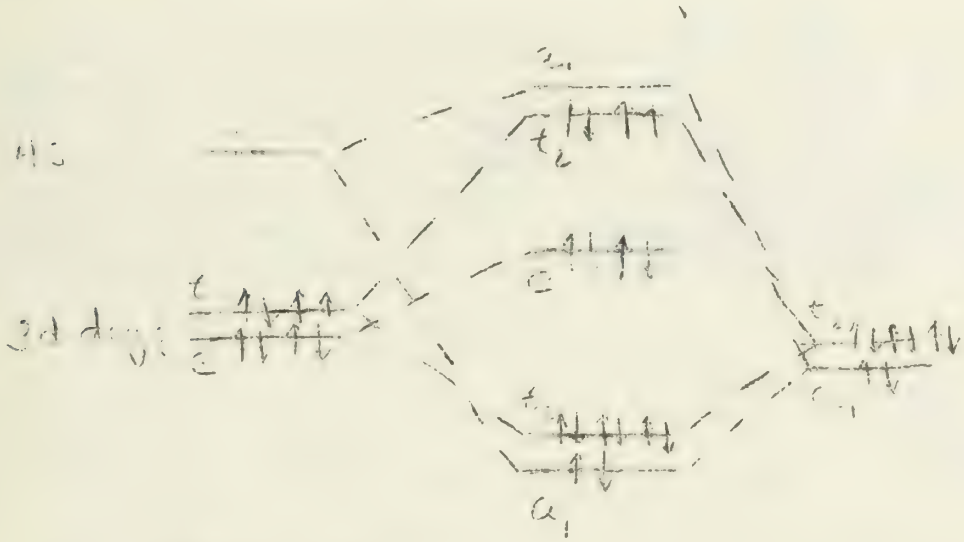
In constructing a molecular orbital scheme due care must be taken to "match" ligand and metal orbitals of the same symmetry. The $NiCl_4^=$ ion has been chosen to demonstrate the method. This ion has been shown to possess nearly, if not exactly, Td symmetry (8). As in the previous section, we first draw the ion with "labelled bonds" and generate a reducible

representation with these, this time for the ligand orbitals. From the four Cl^- sigma bonds we can expect four molecular or symmetry orbitals. (See last page)

(σ orb.) = $A_1 + T_2$

(symmetries of ligand molecular orbitals)

From the character table it is seen that the Ni(II) d orbitals possess E (d_{z^2}, $d_{x^2-y^2}$) and T_2 (d_{xy}, d_{xz}, d_{yz}) symmetries. The s orbital is always totally symmetric. Hence, ligand and metal orbitals of the same symmetry are joined in the diagram and the electrons added (9). Note that this procedure, which is identical to that of the last section, yields the well known sp^3 hybridization for tetrahedral transition ion complexes.



Metal orbitals Ligand orbitals

CRYSTAL FIELD THEORY

Since the maximum M_l for Ni(II) (d^8) is three and there are two unpaired electrons, the ground state term symbol for the free ion is 3F. Due to electronic repulsions there is a 3P level just above the 3F level. Here, the splitting of these states by a crystal field will be considered and then furthur splitting by spin-orbit coupling will be discussed.

The angular portions of the free ion wave functions are spherical harmonics, and, as such, generate the irreducible representations of the full rotation group. The behavior of a member of this group under various symmetry operations of the finite groups is summarized in the following table (10).

$\chi^L(E) = (2L + 1)$

L	C_2	$\chi^L(C_2)$	L	C_3	$\chi^L(C_3)$	L	C_4	$\chi^L(C_4)$
0		1	0		1	0		1
1		-1	1		0	1		1
2		1	2		-1	2		-1
3		-1	3		1	3		-1

The Ni(II) ion in our example is subjected to a T_d field and hence the free ion terms are split. A reducible representation is generated under the T_d character table using the above tables. When decomposed, this reducible representation yields the symmetries of the various energy levels which have arisen as a result of the tetrahedral field. (See last page)

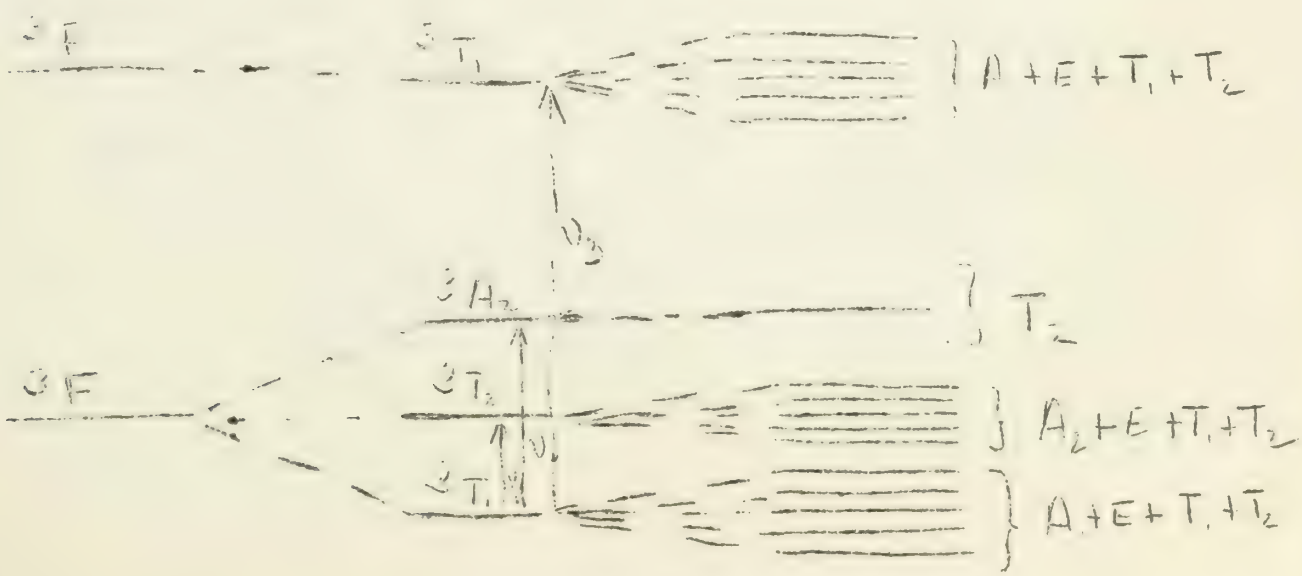
$$\Gamma(\ ^3F) = A_2 + T_1 + T_2$$
$$\Gamma(\ ^3P) = T_1$$

To determine the effect of spin-orbit coupling on these levels, the symmetry of the spin function must be determined. A theorem, valid for integral spins, states that $\Gamma(S = n) = \Gamma(L = n)$. Therefore, the spin symmetry is found in the same manner as the orbital symmetry. For Ni(II), S = 1. The spin-orbit splitting is obtained by forming the direct product and decomposing the reducible representation into the (spin x orbit) irreducible representations. (See last page)

$$\Gamma(S = 1) \times A_2 = T_2$$
$$\text{"} \times T_1 = A_1 + E + T_1 + T_2$$
$$\text{"} \times T_2 = A_1 + E + T_1 + T_2$$

(As a check, the number of new levels must equal $(2L + 1)(2S + 1)$)

It is not possible, at this point, to tell what the order of energy levels is. These must be calculated.



As was discussed in the infrared section, only transitions are allowed which correspond to the transition integral containing the totally symmetric representation. From these considerations, where $R = T_x + T_y + T_z$, three transitions are allowed. The effect of spin-orbit coupling is to split these three bands.

Cotton, et. al., (11) have studied the spectrum of $NiCl_4^=$ and found the ν_2 and ν_3 bands in the visible region of the spectrum. The ν_3 band is quite obviously split (by s-o coupling)into at least four peaks. Liehr and Ballhausen (12) have constructed the E vs. Dq diagram for T_d Ni(II) and Cottonds work agrees very well with theory.

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$	
A_1	1	1	1	1	1	T_z, α_{zz}, α_{xx}, α_{yy}
A_2	1	1	1	-1	-1	R_z
B_1	1	-1	1	1	-1	$\alpha_{xx} - \alpha_{yy}$
B_2	1	-1	1	-1	1	α_{xy}
E	2	0	-2	0	0	$(\alpha_{xz}, \alpha_{yz})(T_x, T_y)$ (R_x, R_y)
	For Normal Modes					
Γ (motion)	18	2	z-2	4	2	
	For Hybrids					
Γ (hyb.)	5	1	1	3	1	

T_d	E	$8C_3$	$3C_2$	$(i\times C_2)$ $6\sigma_d$	$(i\times C_4)$ $6S_4$	
A_1	1	1	1	1	1	$\alpha_{xx}+\alpha_{yy}+\alpha_{zz}$
A_2	1	1	1	-1	-1	
E	2	-1	2	0	0	$\alpha_{xx}-\alpha_{yy}$, $\alpha_{xx}+\alpha_{yy}-2\alpha_{zz}$
T_1	3	0	-1	-1	1	(T_x, T_y, T_z)
T_2	3	0	-1	1	-1	(R_x, R_y, R_z) $(\alpha_{xy}, \alpha_{xz}, \alpha_{yz})$
			For Ligand Molecular Orbitals			
Γ(orb.)	4	1	0	2	0	
			For T_d Field Splitting			
$\Gamma(^3F)$	7	1	-1	-1	-1	
$\Gamma(^3P)$	3	0	-1	-1	1	
			For Spin-Orbit Coupling			
$\Gamma(S=1)$	3	0	-1	-1	1	
" $\times A_2$	3	0	-1	1	-1	
" $\times T_1$	9	0	1	1	1	
" $\times T_2$	9	0	1	-1	-1	

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RECENT REACTIONS OF THE METAL CARBONYLS

L. Jane Park July 17, 1962

In the past two years, developments in the area of metal carbonyls have been quite numerous. The carbonyls are unique for two reasons: first, they are restricted to the transition metals and second, they show a pronounced preference for the low valence states. The object of this seminar is to present a brief review of some of the recent work on carbonyls.

Bonding in the carbonyls involves the overlap of the d, as well as S and P, orbitals of the metal with the π -orbitals of ligands. However, the stability of the carbonyls depends upon back donation from the metals d shell to the ligand. Thus if the carbon monoxide molecule may be written as $C^- \equiv O^+$, complexation with a metal produces $M^- - C \equiv O^+$, and back donation yields M=C=O. The mode of bonding thus indicates the reason for restriction of the carbonyls to the transition metals.

The carbonyls are so varied that it is difficult to classify them. Classification of reactions in this seminar is on the basis of the entering ligand in a given reaction.

I. Hydrocarbons

The added stability of the "mixed" compounds and the preparative techniques involving the hydrocarbons substituted carbonyls are important reasons for the rapid accumulation of data in this area. Both unsaturated ring systems and simple olefins are quite common as ligands in substituted metal carbonyls.

A. Ring Systems

Tropylium tricarbonyl chromium complexes have been studied by Munro and Pauson. In addition to so-called "normal" reactions of this complex (1), they have observed a ring contraction (2) and an intermolecular coupling of the ligand of the complex ion (3). Other tropylium complexes include tricarbonyl tropylium vanadium, in which vanadium formally has an oxidation state of (-1) (4).

Substitution of the sulfur atom by an $Fe(CO_3)$ group occurs when $Fe_2(CO)_{12}$ is reacted with thiophene (5). The process is believed to be related to the mechanism of the metal desulfurization process in organic reactions. A structure is proposed for the product.

Various resonance structures may be written for the biphenylene molecule, one of which includes a cyclobutadiene derivative. However, it has been found that only the six membered rings are utilized in π -bonded complexes (6). When two metal-carbonyl groups are bonded to biphenylene, the resulting structure is believed to be trans, from x-ray studies.

Iron pentacarbonyl has the unusual property that when reacted with 1,5 cyclooctadiene, no organo-metallic compound is formed but rather conjugation of the diene is observed (7). Other non-conjugated dienes have been found to form complexes in which the dienes are conjugated.

B. Simple Olefins

Manganese, cobalt, nickel and palladium carbonyls containing an allyl group have been studied (8). Since the atoms in a π -connected allyl group are found to be coplanar, there are believed to be two isomers possible with terminally substituted allyl groups. The - allyls seem to be more thermally stable than alkyl and aryl derivatives of the metals.

Other workers have studied the protonation of allyl-type complexes, including those of iron, cobalt and manganese with HCl (9). In the case of π -cyclopentadienyl iron dicarbonyl sigma propene (10), addition of the proton causes a unique rearrangement to a cation containing a π -bonded propene group. The reaction is irreversible.

A compound analogous to the above mentioned ones is formed when $Mo(CO)_6$ is reacted with acrylonitrile (11). Analysis data are consistent with the formula $(CH_2CHCN)_2Mo(CO)_2$. A structure has been formulated but is in question because it does not account for the observed insolubility of the product.

Reaction of $Co_2(CO)_8$ with acetylenes followed by acid treatment produces a compound whose stoichoimetry is $[Co_3(CO)_9(C_2H_2R)]$. A structure is proposed which is consistent with infra-red data. The same compound results when $Co_2(CO)_8$ is reacted with tri halogeno methyl derivatives (12).

II. Carbon Monoxide

Much interest has been aroused by the carbonylation reaction because the synthesis of aldehydes, acetals (13) and alcohols (14) are believed to be catalyzed by a cobalt complex formed by insertion of a carbon monoxide group into the coordination sphere. For example, reaction between carbon monoxide, hydrogen and ethyl ortho formate produces 1,1 diethoxy-propane (13). The inserted carbon monoxide apparently becomes part of an aldehyde which then reacts with a molecule of the ortho ester to form an acetal.

Reaction between cobalt carbonyl hydride and olefins produces an alcohol, one of the intermediate steps being carbonylation of an alkyl cobalt tetra carbonyl complex (14). Addition of triphenyl phosphine at 0^oC allows isolation of the acyl intermediate.

Reduction of the silver amine complexes with carbon monoxide is believed to proceed by a carbonylation-type mechanism, in which a carbon monoxide group is inserted into the coordination sphere. The rate law is found to depend upon the concentration of carbon monoxide (15).

Bonding is believed to exist between two different transition metals in a number of carbonyl derivatives (28,29). The first one of these to be observed has the formula $C_5H_5MoC_5H_5W(CO)_6$. Structures are proposed for these substances.

Another type of metal-metal bonding is believed to occur when $Fe(CO)_5$ is reacted with organo-tin compounds (30). The proposed structure contains no tin-tin or iron-iron bonds.

The expected product of the reaction between a platinum metal fluoride and carbon monoxide is a lower fluoride, the carbon monoxide acting as a reducing agent. There have been observed, however, compounds with stoichiometries $Pt(CO)_2F_8$ and $Rh(CO)_2F_3$ (31). The compounds exhibit abnormally high valence states and coordination numbers.

Alkyl manganese pentacarbonyl will react with primary and secondary amines to produce the compound with formula $RCOMn(CO)_4NHR'R''$ (32). Since no carbon monoxide is given off, the mechanism is apparently not a simple displacement. Evidence has been advanced for an amine displacement of the alkyl group followed by attack of the alkyl group on one of the metal-carbonyl ligands. The mechanism is said to resemble a carbonylation-type reaction of alkyl manganese pentacarbonyl.

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ELECTRONIC CONFIGURATION OF TETRAHEDRAL OXYANIONS OF TRANSITION METALS

P. Van Der Voorn July 24, 1962

A number of models have been proposed for the electronic configurations of transition metal complexes in general, and of tetrahedral complexes in specific. It appears that ligand field theory can account for the experimental evidence in a more quantitative manner than any other model.

The first model which could, at least qualitatively, account for the observed spectra of tetrahedral complexes was the Bethe-Van Vleck ionic model. However when an attempt is made to make quantitative predictions, this model soon proves inadequate.

The intensity of a transition is commonly expressed in terms of the oscillator strength which is defined as

$$f = 4.32 \times 10^{-9} \int \epsilon_{\nu} \, d\nu \text{ , i.e. constant X area}$$

In the case of a Gaussian curve this can be approximated as

$$f = 4.60 \times 10^{-9} \; \epsilon_{max} \quad \nu_{1/2}$$

where $\nu_{1/2}$ is the width of the band where $\epsilon_{\nu} = 1/2 \; \epsilon_{max}$
In theory

$$f = 1.085 \times 10^{-5} \nu [\text{av}_{I} \sum_{II} | \int \psi_{I}^{*} \; \vec{r} \; \psi_{II} \, d\tau |^{2}]$$

where ψ_{I} and ψ_{II} are the wavefunctions of the initial and final states, ν is the frequency of the band and

$$\vec{r} = \underline{i}\, x + \underline{j} y + \underline{k}\, z$$

$\text{av}_{I} \sum_{II}$ means summed over the excited states and this sum averaged over the initial states. e.g. if there is a three fold degenerate ground state and a two fold degenerate excited state, there are a total of 6 combinations which are averaged over three, because of the triply degenerate ground state (1).

If the e and t_2 wave functions in the Bethe-Van Vleck ionic model, are composed solely of $(3d)^n$ electronic configurations, no visible electronic dipole transitions are allowed. Vibronic perturbations lead to bands with intensities of only $f = 10^{-4} \sim 10^{-5}$, compared to observed values of $f = 10^{-3}$.

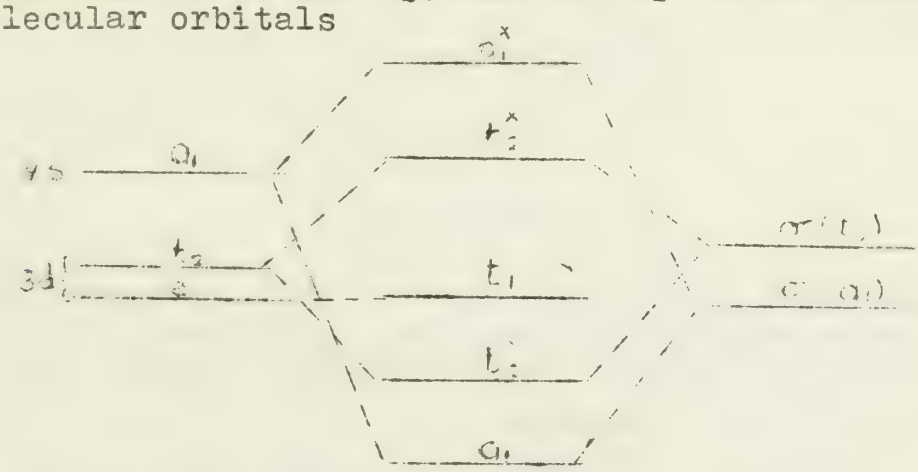
Two alternate mechanisms have been suggested to account for the observed spectra:

1) mixing of 3d and 4p wave functions due to the tetrahedral crystal field, or
2) mixing of 3d and ligand wave functions due to the tetrahedral ligand field.

Assuming mechanism I above, Ballhausen and Liehr calculated

oscillator strengths for two tetrahedral complexes which have been well characterized i.e. $CuCl_4^{=}$ and $CoCl_4^{=}$. There was very poor agreement between calculated and experimental values, hence mixing of 3d and ligand wavefunctions must occur and a molecular orbital model must be used (2).

One such model involves -bonding only. The linear combinations which, through group theory, can be formed from the σ bonds of the four ligands are found to be of a_1 and t_2 symmetry and are combined with the 3d (e and t_2) and 4s (a_1) metal atomic orbitals to form molecular orbitals



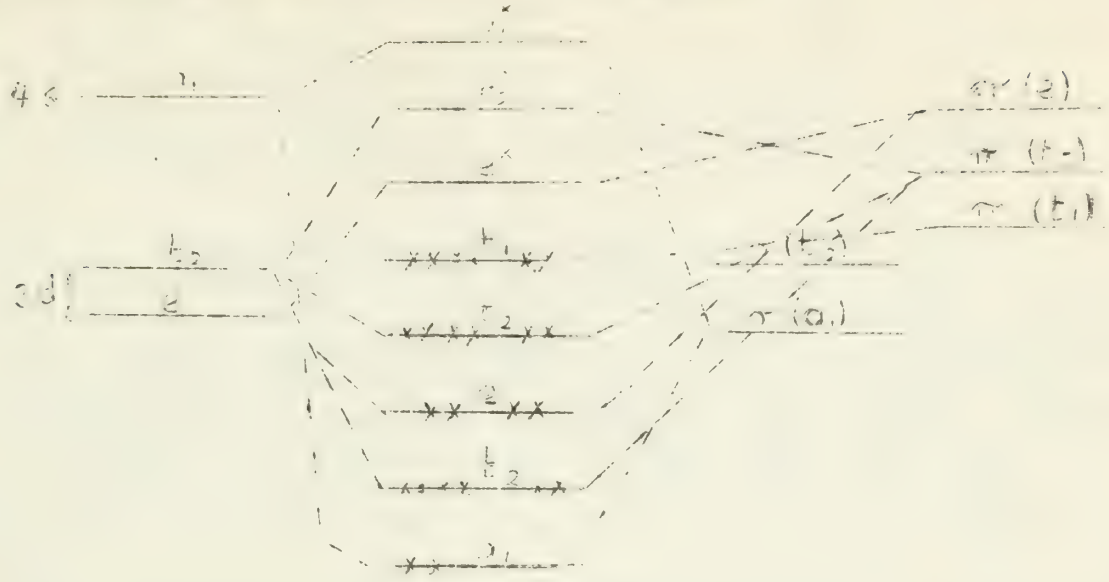
Oscillator strengths calculated for $CoCl_4^{=}$ and $CuCl_4^{=}$, agree quite closely with experimental values but agreement for MnO_4^{-} and $CrO_4^{=}$ is very poor (2).

The next step is to include π-bonding which must play an important role with oxygen as the ligand. The first such model for $CrO_4^{=}$ and MnO_4^{-} was proposed by Wolfsberg and Helmholz(3). Linear combinations of the ligand orbitals lead to combinations of A_1, E, T_2 and T_1 symmetry which are combined with the proper metal atomic orbitals of E, T_2 and A_1 symmetry; T_1 forms a non bonding orbital. Wolfsberg and Helmholz made extensive quantum mechanical calculations in order to find the relative energies of the molecular orbitals and were able to obtain values for the energies of the absorption bands of $CrO_4^{=}$ and MnO_4^{-}, which agree fairly closely with observed values, as shown below:

	MnO_4^{-}		$CrO_4^{=}$	
	obs	calc	obs	calc
1st transition	2.29 ev	1.68ev	3.25ev	2.42ev
2nd transition	3.96ev	2.78ev	4.59ev	3.15ev

The (necessary) oversimplifications led to some surprising results as pointed out by Ballhausen and Liehr (2): Large stabilization of the metal non π-bonding orbital of e symmetry and inversion of bonding energy levels in going from MnO_4^{-} to $CrO_4^{=}$. They proposed an alternate energy level diagram but established the order of the molecular orbitals from chemical intuition and

they did not calculate the relative energies.



The diagram above is that for MnO_4^- or $CrO_4^=$ which have a "closed shell" structure. Oscillator strengths were also calculated for these two ions, with the results below

			f(calc)(2)	f(obs)	
$CrO_4^=$	ν_1	27,000 cm^{-1}	6.7×10^{-2}	8.9×10^{-2}	(3)
	ν_2	37,000 cm^{-1}	0.092	0.11	(3)
MnO_4^-	ν_1	18,500 cm^{-1}	3.9×10^{-2}	3.2×10^{-2}	(4)
	ν_2	32,000 cm^{-1}	0.073	0.07	(4)

In order to arrive at these values, effective nuclear charges had to be postulated, but it was found that the results are rather insensitive to variations in the assumed charges.

The diagram above can be extended even further by including the metal 4p orbitals of t_2 symmetry to give an extra antibonding t_2^* molecular orbital, and the oxygen lone pairs of a_1 and t_2 symmetry to give two extra non-bonding molecular orbitals (5).

In 1939 Teltow(6) suggested that a correlation might exist between the long wavelength absorption edge and the ionic radii for ions with an electronic structure similar to $CrO_4^=$ and MnO_4^-. Carington and coworkers(7) plotted these two quantities for a number of ions and found a straight line relationship for the 3d and 4d transition metals; the 5d transition metals seemed to fall on a separate straight line, possibly because of increasing importance of 5f orbitals in bonding.

A considerable amount of electron spin resonance work has been done on these ions. The first work (8) reported has turned out to be partly in error because the spectra were obtained from samples dissolved in alkali glasses, rather than from single crystals. For the ions MnO_4^-, CrO_4^{3-} and ReO_4^{2-}, all containing one unpaired electron, one line was observed at 20°K. The

line width was highly dependent on temperature which is evidence for spin-orbit coupling. Spectra were also obtained for MnO_4^{3-} and FeO_4^{2-} as well as RuO_4^{2-} and ReO_4^{3-}, but later work on the first pair of ions has disproved the earlier results which appeared to indicate that the two unpaired electrons were present in a triply degenerate orbital, in agreement with the model proposed by Wolfsberg and Helmholz.

FeO_4^{2-} in a K_2CrO_4 crystal gave two lines with little temperature broadening and a g-value (2.000 ± 0.004) equal to the free spin value. This indicates that there are two unpaired electrons in a doubly degenerate molecular orbital. Two electrons in a triply degenerate orbital would give rise to spin-orbit coupling and a g-value considerably different from 2.000. Furthermore, the e^* molecular orbital must be well separated from the lower lying completely filled orbitals and the higher lying unoccupied levels (9). The two lines are a result of zero-field splitting(15).

Similar results were obtained for MnO_4^{3-} in Na_3VO_4 which gave six pairs of lines because the ^{55}Mn nucleus has a spin I = 5/2 (9).

In early work, two peaks were obtained also for RuO_4^{2-} and ReO_4^{3-} both with temperature broadening(8) but these results, similarly to those for FeO_4^{2-} and MnO_4^{3-}, may also turn out to be incorrect when single crystal studies are made.

In the study of MnO_4^{2-} in K_2CrO_4 crystal, six hyperfine lines and some quadrupole lines were observed (9). Quantum mechanical calculations by Schonland (10) show that the experimental results can be explained only on the assumption that the unpaired electron occupies a doubly degenerate orbital. The e^* orbital is largely concentrated in a 3d orbital centered on the Mn atom while the t_2^* orbital is spread out over the whole molecule. Attempts to fit the data to the diagram of Wolfsberg and Helmholz ended in failure.

The spectra of a number of anions had been interpreted by Carrington and coworkers (7) on the basis of the model proposed by Wolfsberg and Helmholz(3) but the above evidence (9,10) in favor of the model of Balhausen and Liehr (2) has prompted them to reconsider their assignments (11). The transitions $t_1 \rightarrow e^*$ and $t_1 \rightarrow t_2^*$ in MnO_4^{2-} are split because of Coulomb effects caused by the presence of one electron in the e^* level. Calculations indicate that the $e^* \rightarrow t_2^*$ transition should be comparable in intensity to the d-d transitions in transition metals, while the $t_1 \rightarrow e^*$ and $t_1 \rightarrow t_2^*$ should be very intense. They further came to the following conclusions:

1. There is strong bonding through the a_1 and t_2 levels which may be compared to the d^3s hybrid orbitals.
2. The unpaired electrons in a doubly degenerate level, are concentrated mainly on the metal ion and hence the electrons in the bonding e level are concentrated mainly in the oxygen atoms. Wolfsberg and Helmholz seem to have overestimated the importance of π-bonding.

3. The intense bands of the visible and UV regions are due to charge transfer transitions from oxygen to metal atoms.

All the evidence presented so far seems to favor the Ballhausen and Liehr model greatly over that of Wolfsberg and Helmholz. However FeO_4^{3-} which has 3 electrons beyond the closed shell structure of MnO_4^- and should therefore have only one unpaired electron according to the Ballhausen and Liehr model, forms an exception. It has been found to have a magnetic moment of 3.6-3.7 B.M. compared to a theoretical value of 3.87 B.M. for three unpaired electrons (12). Lott and Symons (13) have attemptdd to prepare MnO_4^{4-}. containing tervalent Mn which would also have three extra electrons. Although Mn(IV) may have been prepared there was no evidence for a tetrahedral species. For two other ions: FeO_4^{4-} and CoO_4^{4-}, which contain 4 and 5 electrons resp. beyond the "closed shell" structure of MnO_4^-, no magnetic moments have been reported (14).

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THE DEFECT SOLID STATE
AN INTRODUCTORY SURVEY

Violet I. Imhof July 26, 1962

INTRODUCTION

Since the classic x-ray experiments by Laue in 1912 it has been realized that not only are there defects and disorder in the lattices of real crystals but also these imperfections are closely connected with the physical and chemical properties of solids. In this seminar we shall attempt to provide a general survey of this field with emphasis on an understanding of the nature of some of the fundamental defect types, so that the current literature may be read with comprehension. There have been several recent introductory reviews (1,2). More detailed material may be found in references 3-9 and in the series "Solid State Physics". (10)

PHONONS

The motion of atoms in a crystalline lattice is restricted to oscillation about an equilibrium point by the force field of neighboring atoms. The frequency of this mechanical vibration is designated ν_0. For a one dimensional vibration where Hooke's Law holds, the allowed vibrational levels are given by $E_n = (n+ 1/2)\, h\, \nu_0$, where n is a position integer or zero. Thus the energy difference between two states where $n = n'$ and $n = n''$ is $E = E_{n''} - E_{n'} = (n''-n')h\,\nu_0$. The term phonon is given to the minimum $/\Delta E/$, $h\nu_0$ (11).

No interaction between phonons in different vibrational planes would be observed if forces between atoms strictly followed Hooke's Law. The forces are not strictly Hooke's Law forces, however, and interaction does occur. Large amounts of phonon interaction can result in movement of atoms or ions into the lattice to produce vaporization. A smaller degree of interaction can cause the production of free electrons and positive holes or may elevate free electrons to higher energy states in the case of metals or alloys (9). The phonon concept has proven useful for example in treating thermal and electrical conduction (2) and semiconductivity (9).

ELECTRONS AND POSITIVE HOLES

We have just seen that phonon interaction in a crystal in thermal equilibrium can produce free electrons and electron absences (positive holes) in what would normally be an insulator.

These imperfections can also be generated by irradiation, high field conditions, or impurities, among other things. It is these electrons and holes that are the current carriers in semiconductors. They will be discussed more fully in connection with semiconductivity in a later section.

EXCITONS

It would be expected that an electron and positive hole would annihilate each other. It is possible however that prior to this, attraction would lead to the formation of a bound pair. The interaction should be much the same as in the hydrogen atom. The term exciton was first used for this pair by Frenkel (12). Wannier has identified excitons with wave functions and energy levels (13). Using these results Hiller and Marcus (14) showed that in general anisotropy exists in the motion of excitons and that the effective mass of an exciton corresponding to a dipole transition is of the order:

$$m_{eff} \simeq (m_e/f_{n_o}) \quad (R_o/a)$$

where m_e = electronic mass, f_{n_o} = oscillator strength of the corresponding isolated atomic transition, a = equivalent Bohr radius of an internal exciton orbit, $R_o = (3/4\pi n_o)^{1/3}$ and n_o = atomic density. Thus if f is about one and a about 3Å, the exciton mass is approximately the electronic mass. Thus an exciton may either by viewed as a neutral particle produced by partial recombination of an electron and a positive hole or as an excited state of an atom or ion capable of migration from one lattice cell to another.

Experimentally the exciton is infered from peaks on the low energy side of the first absorption band of the crystal. Irradiation with light of the frequency of the first absorption band produces photoconductivity indicating ionization. Irradiation at the frequency of the subsidiary peaks however produces no photoconductivity indicating that the electrons are raised to an excited state below the ionization limit (15,16,17,18).

LATTICE DEFECTS

Of more chemical interest are those types of defects which concern the misplacement, displacement or nonplacement of atoms in the crystal. That is, there are three general classes of lattice defect. a) Atoms or ions may occupy metastable positions off the lattice sites, called interstitial positions. b) Lattice sites may be occupied by foreign atoms. If the impurity atoms are small enough they may also occupy interstitial positions. It is also possible that in a crystal containing A and B, B atoms might be found on A sites and vice versa. This does occur in alloys but is improbable in ionic lattices due to unfavorable electrostatic interactions. c) Lattice sites may be vacant. These positions are termed vacancies rather than holes to distinguish this ionic defect from the electronic defect, positive holes.

Interstial atoms and vacancies may be discussed in terms of two possible kinds of disorder postulated by Frenkel(19) and Schottky(20,21). In the case of a Frenkel defect, ions of one kind may migrate to interstitial positions leaving behind an equal number of vacancies. In general it is the smaller cations which migrate but although it is much less likely anions may also take up interstitial positions. This is termed anti-Frenkel disorder. It is also conceivable that both ions may be found in these positions, this is unlikely and has never been observed. Schottky defects on the other hand do not necessitate interstitial ions. Here the ion migrates to the surface of a crystal, leaving a vacancy behind. To preserve electrical neutrality the number of cation and anion vacancies must be the same.

Although for a given set of conditions one type or another of disorder is apt to predominate, the various types are capable both of separate existence and coexistence. In fact for any real crystal at temperatures greater than 0°K some disorder must exist, for although energy is expended in defect formation, entropy is increased at the same time (22) Accurate knowledge of the energy necessary to form disorders would allow predictions of the type of disorder to be expected in a given case. These calculations have been attempted, but involve many assumptions, particularly about the effect of polarization occurring as a defect is produced (23,24,25,26) Stone gives a comprehensive review in the book by Garner(5). In general Schottky disorder is favored for crystals where ionic sizes are similar and neither the Van der Waals energy nor the dielectric constant are particularly high. The alkali metal halides meet these conditions fairly well, and in general show Schottky defects. Silver halides on the other hand better meet the conditions favoring Frenkel defects, <u>i.e.</u> a large difference in ionic sizes, high Van der Waals energy and dielectric constant.

There are various systems of notation in use. In that due to Rees (27) the nature of the atom occupying a lattice site and the nature of the site are given. Thus $A \mid \square_A$ means an atom of A on an A site. The symbol $A_{1-x} \mid \square_A$ means that the fraction 1-x of the A sites are occupied by A atoms. Similarly, an atom of A in an interstitial position is $A \mid \Delta$. In other notations (1) O represents an interstitial species, $\square$ a vacancy and A•(B) the replacement of B by A. The subscript i may also be used to represent interstitial species.

IMPURITY ATOMS

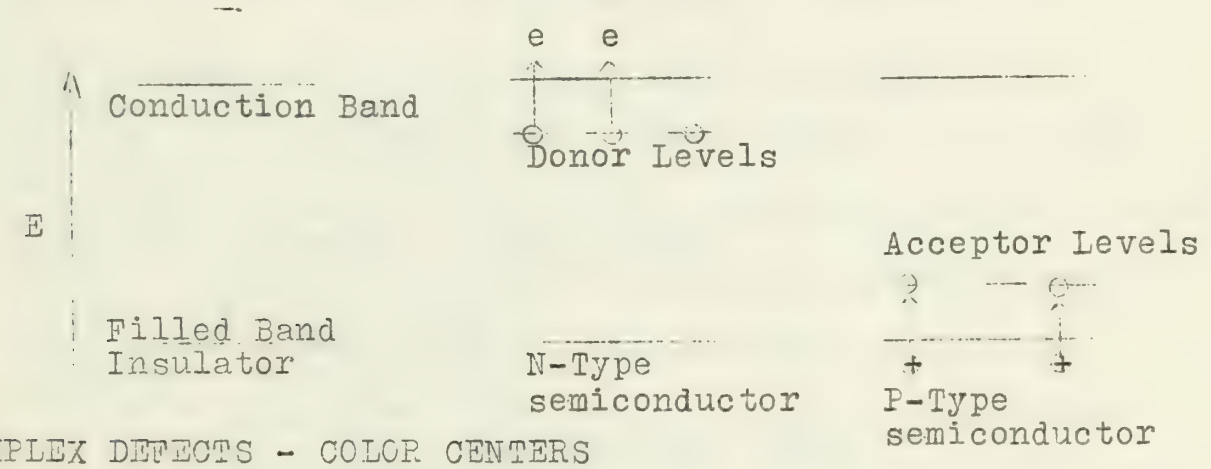
The addition of foreign atoms to a metal lattice changes the number of free electrons. In nonmetals either new electronic levels are produced or existing levels are modified. Extensive reviews on the dependence of crystalline disorder on impurity content are available (6,1).

Here we will only discuss one aspect, semiconductivity.

The classic example is the case of silicon which has the tetrahedral diamond lattice. An arsenic atom added as an impurity can only fit itself into the tetrahedral arrangement by forming an As^+ ion and a free or nearly free electron. The bonding energy of this electron will be decreased by the square of the dielectric constant of the medium. For arsenic in silicon this is 0.09 ev. Hence at normal temperatures the electron is essentially ionized and the material is an N type semiconductor. If boron is used as the impurity atom it must accept an electron from the lattice in order to assume a tetrahedral configuration. This electron borrowing leaves a positive hole behind. The hole is not localized at any particular site and at real temperatures is ionized. Since conduction is by positive holes, this is a P type semiconductor.

The simplest model for the energy levels in insulating materials is shown diagrammatically below. (9) The filled band consists of permitted energy levels separated by a broad forbidden region from the conduction band where the electron is free to move about the crystal. In N type semiconductors there are donor levels a short distance below the conduction band. Electrons from these levels can easily be ionized to the conduction band. In P type semiconductors there are acceptor levels just above the highest filled band. Ionization of an electron from the filled band to an acceptor level leaves a conducting positive hole behind.

In more sophisticated model consideration is given to the existence in the forbidden zone of discrete levels of both donor and acceptor character (28,29). The model due to Morin also considers the effect of d orbitals (30).



COMPLEX DEFECTS - COLOR CENTERS

If a crystal of an alkali halide is heated with alkali metal vapor it undergoes discoloration due to a new absorption band in the visible region (31). This same band is also produced of the crystal is irradiated with x-rays. In this case another absorption also appears in the ultraviolet region (32). These are the F and V bands respectively.

The first model for the defect responsible for the F band, the F center, was proposed by de Boer(33). It pictures a defect consisting of an anion vacancy and a trapped electron. It bears a formal resemblance to the hydrogen atom. If modication is made for the effect of the centers crystalline surroundings and the electronic mass is replaced by an effective mass, calculations using Bohr energy levels give good order of magnitude results for the frequency of the F band. This model is somewhat oversimplified as shown by photoconductivity experiments (34). More detailed analyses have been made of the energetics involved (35, 3a) but the basic model holds. Another defect, the F' center, is believed to be an anion with two trapped electrons. It is produced by irradiation of discolored alkali metal halides with F center light (36).

The V band may also be produced by the alkali halide crystal in halogen vapor. The V centers responsible are formally the enantiomorphs of F centers. Seitz (3c) distinguishes four types of V centers on the basis of recent experimental evidence: V_1, a hole bound to a single cation vacancy; V_3, one hole bound to two cation vacancies; V_2, two holes bound to two cation vacancies; V_4, one hole bound to a unit of an anion vacancy and two cation vacancies.

CONCLUSION

An understanding of the nature of the defect solid state is basic to a grasp of such phenomena, as semiconductivity, luminescence, the magnetic properties of solids and the nature of solid reactions. While it has not been possible to discuss all possible crystal imperfections it is hoped that some insight into the nature of the problem has been provided.

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COMPLEX CHEMISTRY OF PHOSPHINES AND PHOSPHINE OXIDES

William J. Randall October 2, 1962

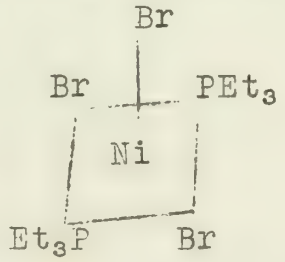
INTRODUCTION

The complex chemistry of ammonia and amines has been known for almost a century. Although the analogous phosphines were available, little characterization of metal complexes of these was done until relatively recently. In the ammonia series, stability decreases with an increase in the number of alkyl or aryl substituents on the nitrogen atom; however, the exact reverse is true in the phosphine series. Although PH_3 will coordinate, it is a strong acid under those conditions and will lose protons readily to form the metal phosphide. An explanation is that the phosphorus atom is large enough to accommodate organic groups and coordinate as well, and the organic groups in turn increase the basicity of the phosphorus by donation of electron density to the phosphorus. This is illustrated in the increasing dipole moment of the series PH_3, PH_2R, PHR_2, and PR_3. The stability of these complexes is illustrated in the ability of the ligand to stabilize unusual oxidation states of certain metals.

PHOSPHINES

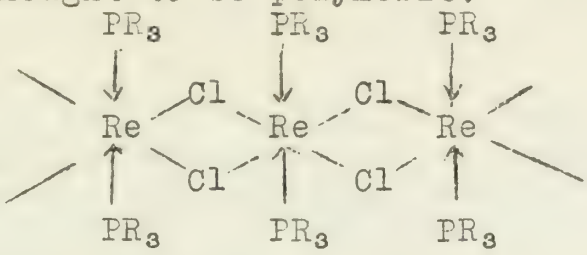
Most of the investigations have dealt with tertiary phosphine complexes. In general, these are made by allowing an anhydrous metal salt to react with the phosphine either in a solvent or in the fused state, followed by filtration of the insoluble complex or extraction and then precipitation, respectively. Such procedures were used in forming complexes of Ru(II) and Os(II) (1). These form dinuclear complexes of the formulea $[Ru_2(PR_3)_6Cl_3]Cl$ and $[Os_2(PR_3)_6Cl_3]Cl$. Chromium forms $[Cr(PR_3)_2X_3]_2$ (X=Cl, Br) from a benzene or toluene solution. (2,3) The halides CrX_2(X=Cl,Br) give $[Cr(PR_3)_2X_2]$, which compounds are fairly unstable and perhaps polymeric. Tertiary phosphines also form compounds with silicon halides of the formula $[Si(PR_3)_2X_4]$(4).

Nickel bromide and triethylphosphine form $[Ni(PEt_3)_2Br_2]_2$ which collects as dark-violet-red crystals. Treatment of this compound with bromine gives a compound which is violet-black in crystalline form and dark green in solution. Dipole moment studies indicate that it has a tetragonal pyramidal structure (in solution)



It is definitely an example of nickel (III) (5).

Using $HReO_4$ and excess PR_3 in ethanol in the presence of hydrohalic acids, Freni and Valenti obtained $Re(PR_3)_2Cl_3$, which upon treatment with hydrazine gives $[Re(PR_3)_2X_2]$(6). The Re(II) compound was thought to be polymeric:



The paramagnetism of the compound corresponds to one unpaired electron, which indicates that the species in solution is square planar with <u>cis</u> chlorides. The $[Re(PR_3)_2X_3]$ compounds are non-electrolytes, very poorly soluble, diamagnetic, and non-reactive toward elemental halogens. Hence the structure is thought to be dimeric with the rhenium atom coordinately saturated. Chatt and Rowe (7) found that the compounds reported to be $Re(PPh_3)_2Cl_3$, $Re(PPh_3)_2Br_2$, and $Re(PPh_3)_2I_2$ were really $ReOCl_3.(PPh_3)_2$, $ReO(OEt)(PPh_3)_2Br_2$, and $ReO(OEt)I_2(PPh_3)_2I_2$, respectively. These workers concluded from their investigations that the formation of "oxo" and "alkoxy" complexes of rehenium is a general phenomenon when alcohol is used as the preparatory medium. Colton and Wilkinson also report a $Re(PPh_3)_2I_4$ (8). Other complexes of tertiary phosphines are reviewed in references 9 and 10.

Thermodynamic studies of the adducts of trialkyl phosphines with diacetyl-bisbenzoylhydrazino-nickel(II), showed them to be 4-11 times as stable as those with trialkyl amines. Triphenyl phosphine would not form an adduct with this metal species owing to the steric interaction of the three phenyl groups with the metal complex. However, the ligands PEt_3, PPr_3, and PBu_3 give $\triangle F$ values of 8.43, 7.85, and 7.85 (kcal/mole), respectively (11).

Triphenyl phosphine with -<u>onium</u> iodomercurate salts-- M_2HgI_4, $MHgI_3$, MHg_2I_5, MHg_3I_8(M = quaternary cation)-- in acetone, or ethanol, forms iodotriphenylphosphine mercury(II) complexes and either an -<u>onium</u> iodomercurate with a higher (iodine/mercury) ratio than the reactant or a quaternary iodide (12). Further reaction of these complexes with alkyl halides gives the corresponding phosphonium halomercurates (13).

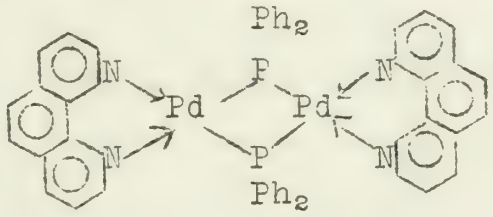
Compounds of the form $[Ag(P(C_6H_{11})_3)_2I]$, $[Ag(P(C_6H_{11})_3)I]$, and $[Ag(P(C_6H_{11})_3)_2SCN]$ have been reported. The latter forms monoclinic crystals of the space group C or C_2/c with cell dimensions $\underline{a}$= 16.80, $\underline{b}$= 9.30, and $\underline{c}$=24.64 (Å), β=108°40', and density = 1.33g./cm³. Cryoscopic measurements in benzene indicate that the compound is a monomer in solution (14).

The compound $P(PhCH_2)Et_2$ and excess $NiBr_2$ in toluene give $[NiBr_2.P(PhCH_2)Et_2]$ (15). The structure of some first-row transition metal phosphine complexes is discussed in reference 16.

The ditertiary phosphines, $R_2P(CH_2)_nPR_2$, are analogous to alkylene diamines and form similar complexes (10,17,18,19,20). Also reported are complexes of the general composition $[M(Ph_2P\text{-}PPh_2)_2\text{-}X_2]$, which are made from $NiBr_2$, $PdCl_2$, $CoBr_2$, CoI_2, (21 ,22) and Cu_2Br_2(21).

A departure from the ordinary synthetic route is seen in the mixing of $P(PhCH_2)_2H_2^+Br^-$ and K_2PdBr_4 in aqueous-alcoholic solution, which gives the product $[Pd(P(PhCH_2)_2H)_2Br_2]$ (pale yellow crystals) (23). The preparation of other secondary phosphine complexes and primary phosphine complexes is analogous to that described above.

The compounds $PHPh_2$ and $CoBr_2$ give three products which are thought to be $[Co(PHPh_2)_3Br_3]$, $[Co(PHPh_2)_3Br]Br$, and $[(PHPh_2)_4\text{-}Co(Br)_2Co(PHPh_2)_4]Br_2$. The corresponding nickel bromide gives $[Ni(PHPh_2)_2(PPh_2)_2]$, and with $PHEt_2$ gives $[Ni(PHEt_2)_4Br_2]$(24). The reaction of $PHPh_2$ on palladium halides or halopalladates produces $[Pd(PHPh_2)(PPh_2)X]_2$, (a), and some $[Pd(PHPh_2)_2X_2]$, (b), (X=Cl,Br, I) and $[Pd(PHPh_2)_2(PPh_2)_2]$, (c). The bromide also forms $[Pd(PHPh_2)_3Br]Br$, (d). The tendency to form complexes containing the anionic ligand (PPh_2^-) decreases in the order Cl > Br > I. The presence of hydrohalic acids opposes the formation of these species and favors the dihalide complex--excess $PHPh_2$ favors the formation of (a) and (c) in alcohol and (d) in benzene. The use of alcohols as solvents favors the formation of (a) and (b). Compound (a) is a dimer which does not undergo ligand exchange with PPh_3, but does with orthophenanthroline to form (26)



Primary phosphine complexes with CoX_2(X=Cl, Br, NO_2) are thought to be tetrahedral, and other complexes have the following geometries: $[Co(PH_2Ph)_4I_2]$, octahedral; $[Co(PH_2Ph)_3I]$, trigonal bipyramidal; $[(PH_2Ph)_2ClPd\text{-}PPh\text{-}Pd(PH_2Ph)_2Cl]$, binuclear (square planar Pd). Those of chromium are like those containing the $PHPh_2$ ligand. Copper(I) chloride forms a tetramer, $[Cu(PH_2Ph)Cl]_4$ (27).

PHOSPHINE OXIDES

Pickard and Kenyen reported a phosphine oxide compound of iron in 1906 (28). However, insufficient understanding of complex chemistry was available for a reasonable explanation of the structure. Divalent and trivalent chromium form $[Cr(OPEt_3)_2Cl_2]$ and $[Cr(OPR_3)_3(SCN)_3]$, respectively. These are non-electrolytes, as proved by conductivity and molecular-weight measurements (29). Complexes of trivalent vanadium(30) and nickel(II) bromide (31) have also been characterized. Tri-n-octylphosphine oxide forms a complex with thorium, which allows thorium(IV) to be separated from sulfates (32). Some first-row transition metal complexes with phosphine oxides are discussed in reference 16.

UNUSUAL PRODUCTS

Phosphines have been used to stablize some hydrido (33), organometallic (34-38) and carbonyl (39-54)compounds. The compounds $(Et_2P\text{-}AlCl_2)_3$ and $(Et_2P\text{-}AlCl_3{:}OPCl_3)$ (55) have also been described.

SUMMARY

Phosphines and phosphine oxides as ligands provide an area of complex chemistry that is characterized by highly colored compounds, some of which have quite unusual structures and oxidation numbers.

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SOME SELECTED USES OF OPTICAL ROTATORY DISPERSION IN COORDINATION CHEMISTRY

L. J. Boucher October 9, 1962

INTRODUCTION

The octahedral configuration of certain hexacoordinate complexes implies the existence of mirror-image isomers, and hence optical activity (the ability of single molecules to rotate plane polarized light). This possibility was experimentally realized in 1911 by Werner when he resolved the $[Co(en)_2NH_3Cl]^{2+}$ complex. Thus at the very heart of Werner's theory of coordination compounds lies the phenomenon of optical activity and with it the experimental measurement of the angle of rotation, ψ. It has since become customary to measure the change of rotation with wavelength of incident light. This is known as Optical Rotatory Dispersion (O.R.D.).

The measurement of O.R.D. has steadily grown in importance and today its importance as a research tool is evidenced by the keen interest in it shown by coordination chemists both here and abroad. Although O.R.D. does not have as wide an application to inorganic chemistry as other physical methods such as N.M.R., I.R., and electronic absorption spectroscopy, it does have enough important applications to warrant at least a cursory knowledge of its fundamentals by inorganic chemists and in particular by those concerned with coordination.

The theoretical aspects of the optical rotatory power of transition-metal complexes will not be dealt with here other than to say that such theories do exist (quantum mechanical as well as classical) which purport to relate the optical rotatory power to fundamental mechanical properties of the molecule under consideration. The present state of these theories is somewhat unfinished, but for those who are interested in further pursuit, the references noted provide a starting point: Moffit(2), Sugano(3), Liehr(4), and Piper(5).

A molecule may possess optical rotatory power if and only if it is non-superimpossible upon its mirror image. This is equivalent to saying that an active molecule can neither have a center nor a plane of symmetry. Lowery(6) has used the term "dissymmetric" for figures possessing axes of symmetry but no planes center of symmetry and no alternating axis of symmetry. Dissymmetric figures are not necessarily assymmetric. The simple Drude equation(7) expresses the variation of rotatory power with the wavelength of plane polarized light:

$$[\alpha] \approx \sum_i \frac{k_i}{\lambda^2 - \lambda_i^2} \qquad (1)$$

where k_i is a constant and λ_i is the wavelength of the maximum absorption of the optically active absorption band. The observed

rotation α is experimentally determined. It is related to the specific rotation $[\alpha]$ by the following expression

$$[\alpha] = \frac{100}{dc} \cdot \alpha \qquad (2)$$

where d is the cell length in decimeters and c is the concentration of optically active substances in gr./100 ml. of solution. In the literature, O.R.D. curves are usually plotted in terms of the molecular rotation [M] which is related to $[\alpha]$ by the following expression:

$$[M] = \frac{[\alpha]\ (\text{Mol. wt.})}{100}. \qquad (3)$$

Equation (1) is satisfactory when λ is far removed from the wavelength of the optically active absorption band. If it is within the absorption band, a more complicated expression must be used.

According to Djerassi(8), there are three types of O.R.D. curves: (1) plain curves with no maximum or minimum corresponding to the Drude equation; (2) single Cotton-effect curves with only one maximum and one minimum; and (3) multiple Cotton effects with two or more peaks and troughs. The rapid increase and reversal of sign of optical rotatory power with changing wavelength in an absorption band is known as an anomalous dispersion or as the Cotton effect when associated with a particular electronic transition.

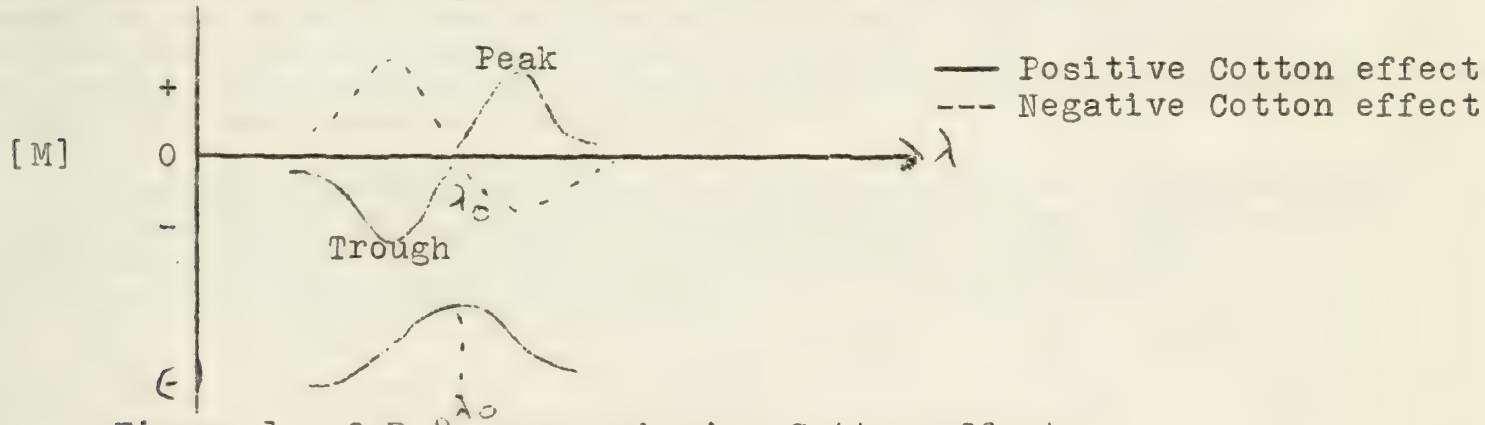


Figure 1 - O.R.D. curve showing Cotton effect.

Figure 1 represents an ideal case in which the observed rotation is due to a single electronic transition and there are no contributions to the rotatory dispersion from other bands. The center of inverstion, λ_0, usually coincides with the wavelength of an absorption maximum. The absorption band is commonly referred to as an optically active absorption band. Both a chromophore and an optically active center must be present within a molecule to produce the Cotton effect. The chromophore may be at the center of activity, or the chromophore and active center may exist in different parts of the molecule, provided there is an interaction between them. The latter condition is called the vicinal effect and will be discussed below.

ASSIGNMENT OF CONFIGURATION

A knowledge of the relative configurations of optical antipodes is of great importance in determining stereochange in some substitution reactions at octahedral metal sites. An example of this is the reaction of l-cis$[Co(en)_2Cl_2]^+$ with ethanol and hydrogen fluoride in a 1:1 ratio in the presence of silver carbonate to form d-cis$[Co(en)_2F_2]^+$[9]. It should be emphasized that the sign of rotation cannot be used to determine relative configuration. The d or l that is usually quoted in the literature tells only whether an optical antipode gives a positive or negative rotation of plane polarized light of a certain wavelength (usually the sodium D line). In the above example the O.R.D. curves of the reactant and product are very similar, leading to a postulated retention of configuration instead of an opponent inversion. Although O.R.D. measurements alone cannot determine relative configuration, it is possible to assign relative configurations, and even absolute configurations when they are used in conjunction with special x-ray crystallographic techniques.

Pioneer work by Mathieu on O.R.D. measurements of a number of cobalt complexes of the general formula d-cis$[Co(en)_2AA^1]^{n+}$ with A and A' = NH_3, H_2O, Cl^-, NCS^-, Br^-, NO_2^- or AA' = CO_3^{2-}, OX^{2-}; the complexes d-cis $[Cr(en)_2Cl_2]Cl$, d-$[Co(en)_2OX]Cl$ and d-cis $[Ir(OX)_2Cl_2]$(10); and $[Me(en)_3]^{3+}$, $[Me(OX)_3]^{3-}$, with Me = Cr^{3+}, Rh^{3+} AND Ir^{3+} (11). He showed that complexes of similar composition which had O.R.D. curves with the same sign and some general shape of the Cotton effect for similar electronic transitions possess the same configuration, whereas if the slopes of the dispersion curves are of opposite sign, the configurations are opposite. Mathieu's postulate was made in conjunction with Werner's solubility rule, i.e., for analogous complex ions, the enantiomorphic forms which produce the less soluble salts with a common resolving agent are considered to have the same generic configuration.

The absolute configuration of an antipode can be determined by special x-ray crystallographic techniques alone. The experiments of Saito and coworkers (12) indicate the absolute configuration of 2-D$[Co(en)_3]Cl_3.NaCl.6H_2O$ to be D(+).

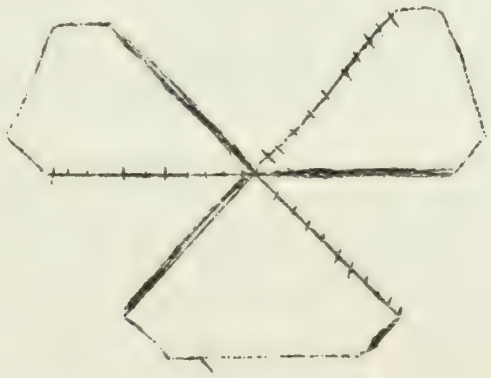


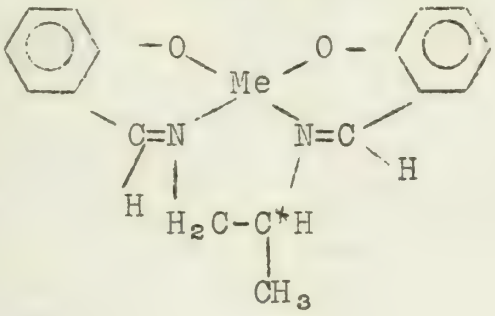
Figure 2. - Absolute configuration of D(+)$[Co(en)_3]^{3+}$.

This figure represents D(+) complex cation, which possesses D_3 symmetry (three fold axes out of plane of paper). If the enclosed areas in Figure 2 are considered as blades of propeller and the

darkened lines as the leading edges of the three propellers. Clockwise rotation of the figure about its three-fold axis shows that the blades will be driven away from the viewer. If the dashed lines and darkened lines are interchanged with those opposite them and the same procedure is carried out the blades now move toward the viewer. The former is called a left-handed system and the latter a right-handed system. Piper(13) has proposed that the left-handed system be designated Λ and the right handed system be designated Δ. The absolute configuration of other $[Me(en)_3]^{3+}$ complexes may now be determined by simply reoording O.R.D. curves and comparing the sign of the Cotton effect for similar electronic transitions. With more and more x-ray determinations being carried out and with the help of O.R.D. measurements, the assignment of absolute configurations to a host of complexes will be possible.

COMPLEXES WITH OPTICALLY ACTIVE LIGANDS

Pfeiffer (14) prepared square -planar complexes of Cu(II) and Ni(II) of the following formulations:



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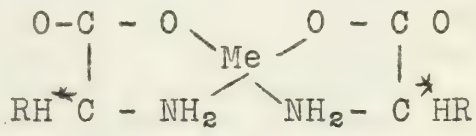

II

In these, the ligand was optically active. In each case the O.R.D. curves showed strong Cotton effects. Neither of the ligands itself showed any Cotton effect in the wavelength range investigated. Mellor (15) proposed that the electronic transition giving the Cotton effect was due to a metal-ligand bond chromophore (Me-N). The absorption band is optically active because of the so-called vicinal effect (16). Since the metal itself is not the site of the optical activity, the asymmetric carbon in the ligand must interact with the chromophore, making the absorption band optically active.

The essential nature of this interaction or coupling is still unknown. The effect is noted even when the asymmetric carbon is removed beyond the position adjacent to the chromophore. Pfeiffer and Christeliet (17) applied this effect to measure the O.R.D. of some Cu(II) complexes of naturally-occurring optically active α-amino acids. The O.R.D. curves for all the complexes (similar to Structure II) and the observed Cotton effects were similar in shape and were in the same region of the spectrum. It was thus shown that the configuration of the asymmetric centers in the different acids is the same and hence that all natural amino acids have the same configuration. Recently the same technique was applied in an attempt to determine the relative configurations of α-amino acids with more than one center of assymmetry (18). The

data did not allow an unambiguous conclusion as to the configuration of the amino acids, but it was possible to correlate the relative configurations of the Δ asymmetry with the shape and the position of the Cotton effects.

In those cases where an optically active ligand (A-A) is in a complex of the type $[Co(A\text{-}A)_2B_2]^{n+}$, both the cis and trans forms are optically active and show Cotton effects near the first absorption band. The optical activity in the trans isomer is due to the vicinal effect of the asymmetric center on the ligand. Inasmuch as the optical activity is due mainly to the arrangement of the groups about the central atom, O.R.D. curves of complexes of similar (cis) configurations should have the same characteristics whether the coordinating base is optically active or not, (e.g., l-propylenediamine versus ethylenediamine). The trans configuration, on the other hand, will show a greatly different O.R.D. curve, since the activity arises from the presence of the optically active base.

Bailar(19) and McReynolds(20) used O.R.D. measurements to assign a cis configuration to $[Co(l\text{-}pn)_2Cl_2]Cl$ and $[Co(l\text{-}pn)_2(NO_2)_2]NO_2$ and a trans configuration to $[Co(l\text{-}pn)_2(NH_3)_2]Cl_3$ on the basis of the striking similarity of the curves of the first two complexes to those of d-cis$[Co(en)_2Cl_2]Cl$ and d-cis$[Co(en)_2(NO_2)_2)NO_2$. The latter complex was assigned a trans configuration because of the dissimilarity of O.R.D. curves to that of the corresponding ethylenediamine complex d-cis$[Co(en)_2(NH_3)_2]Cl_3$. This sort of analysis requires a knowledge of the O.R.D. curves of analogous compounds which can exist in a active form only in the cis configuration. The same procedure was used to assign the trans configuration to $[Co(l\text{-}pn)_2NH_3Cl]Cl_2$ and $[Co(l\text{-}pn)_2(NCS)_2]Cl$(21). It was also found that the O.R.D. curve was inverted by replacing l-pn by d-pn in trans- $[Co(l\text{-}pn)_2(NH_3)_2]Cl_3$, therefore showing that the optical activity of the complex is intimately connected with the optical activity of the base.

In order to investigate the nature of the induced asymmetry that arises when propylenediamine (and other optically active amines) coordinates with a metal that in itself is not dissymmetric, O'Brien and Tool (22) measured O.R.D. curves of Zn^{2+}, Cd^{2+}, Ag^{+}, and Pt^{2+} -l-propylenediamine complexes in the visible region of the spectrum. The curves showed no Cotton effects and could be described by a single one-term Drude equation (one optically active electronic transition in the far ultraviolet). The dispersive power was found to be independent of the metal and the nature of the optically active amine, but dependent on the formation function n. It was concluded therefore that the activity of the complex arises only from the ligands and not from any induced asymmetry around the central atom.

ABSORPTION SPECTRA

Hidaka and coworkers claim that in order to understand fully the nature of absorption bands and especially their splitting and overlapping, O.R.D. curves must be carefully analyzed. When studying the complexes D-cis$[Co(en)_2Cl_2]Cl$ and D-cis$[Co(en)_2(NO_2)_2]Cl$, they found that the Cotton effect corresponding to the first absorption

band is actually a multiple Cotton effect made up of the superposition of two Cotton effects of the same or opposite sign and the tail of a Cotton effect in the far ultraviolet. The multiple Cotton effects are of equal magnitude and arise because of the splitting of the first absorption band into components I_a and I_b. The second absorption band gives rise to only one Cotton effect (of lesser magnitude than the first). Further studies (24) of the complexes D- $Na_2[Co(EDTA)NO_2]$, D-K[Co(EDTA)], D-K_2[Co(EDTA)Cl], and D-cis[$Co(en)_2(NO_2)_2$]I lead to the same results, i.e., the first absorption-band splitting gives rise to a multiple Cotton effect. These workers also reported that D-cis[$Co(en)_2(NO_2)_2$]I shows only one Cotton effect at the first absorption band, which may in fact be a superposition of two Cotton effects of the same sign that are too close together for resolution. The observed absorption spectrum of D-K[Co(EDTA)] does not show any splitting in the first absorption band due to the diffuseness of the bands.

In a later paper, Hidaka and coworkers (25) studied the complexes D-Na[$Co(en)(OX)_2$] and D-K[Co en(Malo)$_2$]. The multiple Cotton effect was also observed for the split first absorption band and a single Cotton effect for the second absorption band. Shimura(26) observed the same result with an optically active ligand where the metal atom is not in the site of activity in the complex. The O.R.D. curve for $[Co(NH_3)_4$(l-leuc)] $(ClO_4)_2$ exhibited multiple Cotton effects of opposite sign near the first absorption band. These can be attributed to the vicinal effect between the cobalt atom and the asymmetric carbon of the amino acid. It was also found that D-[$Co(en)_2$l-leuc]$^{2+}$ has a rotational power greater than D-[$Co(NH_3)_4$ l-leuc]$^{2+}$ and shows only one Cotton effect at the first absorption band. It seems probable that the dissymmetry around the central cobalt atom contributes more profoundly to the rotatory power in the region of the first absorption band than the asymmetric carbon atom in the coordinated ligand. Neither complex shows any Cotton effect in the vicinity of its second absorption band. It also was noted that the center of inversion (wavelength where the Cotton effect crosses the zero rotation axis) was almost always in the longer wavelength region in comparison with the position of the absorption maximum. Some representative data for this section are listed in Table I.

MISCELLANEOUS

There are many other less broad applications of O.R.D. to coordination chemistry cited in the literature, some of which deserve mention. Albinak and coworkers (27) have found that the change in O.R.D. of a dissymmetric complex ion when the optically inactive counter ion associated with it is changed can be related to the degree of ion pairing. Larson (28) maintains that by studying the varation of O.R.D. with concentration of counter ion, the nature of the forces responsible for the association effects or upon the coordination sites preferred by the different ligands can be decided. Kling (29) and Woldbye (30), in a study of the effect of differences between similar chelates on O.R.D. of complexes, report that when ethylenediamine is replaced by trimethylenediamine

Table I. Comparison of Center of Inversion and Absorption Maximum for Some Cobalt Complexes. (First Absorption Band)

Compound		$\nu_{abs.}$*	$\nu_{rot.}$*	Cotton Effect	Ref.
D-cis[$Coen_2Cl_2$]Cl	Ia	49.5	48	-	23
	Ib	57.5	57	+	
D-cis[$Co(en)_2ClNO_2$]Cl		60	55	-	23
		(60)	(55)	-	
D-Na_3[$Co(EDTA)NO_2$]		51.4	49	-	24
		60.4	59	+	
D-K[Co(EDTA)]		55.9	51.5	-	24
			61.0	+	
D-CisK_2[Co(EDTA)Cl]		52.0	51.8	-	24
			57-63		
D-Cis[$Co(en)_2(NO_2)_2$]I		65.5	69	+	24
		(65.5)	(69)	+	
D-Na[$Coen(OX)_2$]		55.6	52	-	25
			60	-	
D-Na[$Coen(Malo)_2$]		55.6	50	-	25
			56.0	+	
[$Co(NH_3)_4$(l-leuc)]$(ClO_4)_2$		60.8	54.6	+	26
			64.6	-	
D-[$Co(en)_2$(l-leuc)]$(ClO_4)_2$		61.5	59.5	+	26

* ν in units of 10^{13} sec^{-1}

$[Co(en)_3]^{3+}$ and $[Cr(en)_3]^{3+}$, the molecular rotation contributed to the first absorption band is reduced by a factor of between 5 and 10 even though the absorption spectra are almost identical. In work being done in the new field of bio-inorganic chemistry, O.R.D. has been used to study the interaction of metal ions with sites in hemoproteins(31) and metalloproteins (32).

CONCLUSIONS

This seminar has attempted to show the importance of O.R.D. in solving structural problems in coordination chemistry. The theory and measurement of circular dichroism, a closely related topic has not been mentioned since this would require another seminar of equal length (for an introduction to this topic see Jaegen (33).

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FAR INFRA-RED ABSORPTION OF TRANSITION-METAL COMPLEXES

Michael R. Rosenthal October 16, 1962

INTRODUCTION

In the last 10 years, a great deal of investigation has been carried out in the far infra-red region. This region, extending from approximately 20-200 μ (50-500 cm^{-1}), had been relatively little investigated earlier owing to instrumental difficulties. These difficulties included low energy, atmospheric absorption, and stray radiation. Raman data were used along with infra-red data in the "fundamental" region for pertinent problems. Fortunately, techniques have now been developed which allow accurate spectra to be determined rapidly in this region. The information gathered has been particularly valuable in structure determinations, bonding studies, and in developing analytical techniques. The far infra-red is much more sensitive to changes in structure than the "fundamental" region, often allowing the difference of only a methylene group to be detected. Heavy-atom stretching frequencies and bending frequencies are usually found in this region. The purpose of this discussion is to review the uses and limitations of the far infra-red and to illustrate its applications to transition-metal chemistry.

APPARATUS

The development of the double-beam double-pass instrument has almost eliminated the problem of stray radiation. The drawback, however, is that this produces a greater energy loss than a single-beam instrument. Flushing with dry nitrogen has eliminated the problem of atmospheric water-vapor absorption. References (1) and (2) discuss apparatus in detail.

Grating spectrometers are useful for very low wavelength measurements (below 250 cm^{-1}). Duncanson, (4), discusses the construction and use of such an instrument. Orr(5) discusses recent advances in infra-red instrumentation.

PHASE

Carbonyl compounds and cyclopentadienyl complexes are generally observed in the gas phase. The procedure usually comprises sealing the compound <u>in vacuo</u> in gas cells and placing in a heating jacket(1).

More commonly encountered are liquid or solution spectra, the latter of which are best obtained with a double-beam instrument, using the pure solvent as the reference. However, if solvent absorption is high (75%), only small differences between large numbers result and much difficulty follows. Well-matched cells are an important criterion. The use of the wedge cell has helped alleviate this difficulty. Reference (2) contains detailed information on solvents.

Solid-state techniques enjoy wide popularity. Mulling the compound in mineral oil or hexachlorobutadiene is common. A drawback to the mull method is that energy tends to fall off at shorter wavelengths (Tyndall Effect). The sample may also be pressed into KBr, CsBr, or CsI discs. Meloche and Kalbus(3) discuss sources of error in this method as a result of anion exchange, pressure, and orientation effects. Occasionally either a powder or film on halide windows or single-crystal work is reported.

It should be kept in mind that shifts due to physical state are larger in this region than at higher wave numbers.

OPTICS (1,2)

To be useful, a prism must transmit the radiation used and give high dispersion. That is, the rate of change of refractive index with wavelength must be large. The following is a table of approximate values of prism ranges

KBr	15-27 μ	370-665 cm.$^{-1}$
CsBr	24-38 μ	265-415 cm.$^{-1}$
TlBr, TlI } KRS-5	24-40 μ	250-415 cm.$^{-1}$
CsI	24-50 μ	200 cm.$^{-1}$-415 cm.$^{-1}$
Grating	50-200 μ	50-200 cm.$^{-1}$

VIBRATIONAL SPECTRA IN DIATOMIC MOLECULES (1)

Before proceeding to specific data, it seems worthwhile to discuss briefly the theoretical considerations of vibrational spectra. A diatomic molecule behaves as a harmonic oscillator in which

$$E = Hr\ (n + \frac{1}{2})$$

where n is the vibrational quantum number. As the molecule vibrates, the dipole moment vector changes with the same frequency. If the molecule is bathed with radiation, the dipole moment vector will "lock in" with the electromagnetic vector of the same frequency, thus allowing for absorption and emission. The process may be expressed as follows:

$$\triangle E = hr(n + 1 + \frac{1}{2}) - hr(n + \frac{1}{2}) = hr$$

Molecular vibrations are found in the infra red from 1-200 μ. (50-10,000 cm.$^{-1}$) If as the molecule vibrates, polarizability changes with the frequency of the vibration, it will show the Raman effect.

The procedure is to bathe the molecule with monochromatic radiation of a frequency much higher than its vibrational frequency. Most of the radiation will be scattered, but now and then a

Solid-state techniques enjoy wide popularity. Mulling the compound in mineral oil or hexachlorobutadiene is common. A drawback to the mull method is that energy tends to fall off at shorter wavelengths (Tyndall Effect). The sample may also be pressed into KBr, CsBr, or CsI discs. Meloche and Kalbus(3) discuss sources of error in this method as a result of anion exchange, pressure, and orientation effects. Occasionally either a powder or film on halide windows or single-crystal work is reported.

It should be kept in mind that shifts due to physical state are larger in this region than at higher wave numbers.

OPTICS (1,2)

To be useful, a prism must transmit the radiation used and give high dispersion. That is, the rate of change of refractive index with wavelength must be large. The following is a table of approximate values of prism ranges

KBr	15-27 μ	370-665 cm.$^{-1}$
CsBr	24-38 μ	265-415 cm.$^{-1}$
TlBr, TlI } KRS-5	24-40 μ	250-415 cm.$^{-1}$
CsI	24-50 μ	200 cm.$^{-1}$-415 cm.$^{-1}$
Grating	50-200 μ	50-200 cm.$^{-1}$

VIBRATIONAL SPECTRA IN DIATOMIC MOLECULES (1)

Before proceeding to specific data, it seems worthwhile to discuss briefly the theoretical considerations of vibrational spectra. A diatomic molecule behaves as a harmonic oscillator in which

$$E = Hr\ (n + \frac{1}{2})$$

where n is the vibrational quantum number. As the molecule vibrates, the dipole moment vector changes with the same frequency. If the molecule is bathed with radiation, the dipole moment vector will "lock in" with the electromagnetic vector of the same frequency, thus allowing for absorption and emission. The process may be expressed as follows:

$$\triangle E = hr(n + 1 + \frac{1}{2}) - hr(n + \frac{1}{2}) = hr$$

Molecular vibrations are found in the infra red from 1-200 μ. (50-10,000 cm.$^{-1}$) If as the molecule vibrates, polarizability changes with the frequency of the vibration, it will show the Raman effect.

The procedure is to bathe the molecule with monochromatic radiation of a frequency much higher than its vibrational frequency. Most of the radiation will be scattered, but now and then a

quantum will be absorbed, and the molecule will go to a higher energy state. It will then re-emit the energy as a quantum of lower energy than the incident radiation. This technique is valuable for some modes of vibration.

Although emission spectra are useful, we usually are more interested in absorption spectra resulting because the Boltzmann distribution favors the lower state. Overtones appear if Δn is larger than 1, and we try to avoid these by proper sample preparation. For a diatomic molecule

$$r = \frac{1}{c}\left(\frac{K}{4\pi^2 \mu}\right)$$

where μ = reduced mass, K = bond force constant, c = velocity of light, and r = oscillator frequency.

VIBRATIONAL SPECTRA OF POLYATOMIC MOLECULES (1)

The problem becomes much more complicated when a polyatomic system is considered. If there are n atoms, there are $3n$ degrees of freedom, of which 3 are translational and 3 (non-linear) or 2(linear) are rotational. Since these 6 (or 5) do not change the relative positions of the atoms there are $3n$-5 (linear) or $3n$-6(non-linear) normal vibrations in a molecule of n atoms. A normal vibration is formally defined as one in which there is no change in the center of mass or angular momentum of the molecule. If an experimental frequency is known for a vibration along with molecular parameters, the bond force constant may be calculated. Herzberg (6) discusses this situation.

The mass effect is worthy of mention. If co-ordination occurs through the apex atom of a triatomic molecule, the motion of that atom will be restricted. Therefore, the frequency shift upon complexation will be greatest for that atom which moves more when uncomplexed. For this reason, H_2O exhibits a small shift when compared to NO_2. This is due to the fact that N motion in NO_2 is greater than O motion in water, which in turn depends on the fact that H (in H_2O) is so much lighter than O (in NO_2).

Group frequencies are valuable in assigning vibrations (101). However, we must realize that often interactions will occur between vibrations of the same symmetry (coupling). These lead to unexpected values. In many cases, a "pure" stretching or bending frequency will not exist. If, however, a bond is very strong, coupling may not occur even if symmetry permits. Carbonyl and nitrile frequencies illustrate this point.

As a molecule becomes larger, analysis becomes more and more complicated. Purcell(7) and references therein apply group theoretical analysis to complicated molecules.

VIBRATIONAL SPECTRA OF COMPLEXES (1)

Several empirical rules may often be applied carefully to spectral analysis of complexes: (a) Ligand frequencies and force constants will not usually vary greatly from free to bound

ligand; (b) Vibrations of bound ligands will not normally couple strongly to vibrations of other ligands or to skeletal vibrations; (c) Slight coupling of ligand vibrations to other molecular vibrations will not usually destroy degeneracies inherent in the free ligand.

OTHER REFERENCES

Lawson(8) contains sparse information on this subject. Bentley and Wolfarth (9) list spectra-structure correlations for a large number of aliphatic and aromatic hydrocarbons. Miller, et al (10), list spectra-structure correlations for 208 inorganic salts containing polyatomic ions. Ferraro (49) discusses inorganic infra-red spectroscopy, though little of the material relates to the far infra-red.

Tabulated below is far infra-red data on transition-metal complexes. Because of space limitations, interpretation of this data is not included. This may be secured from the listed references.

Class and Reference	Compound	Vibration (cm^{-1})	Assignment	Phase	C[illegible]
Thiocyanate(11)	$(NH_4)_3V(NCS)_6.4H_2O$	478	NCS bend	mull, solution	KBr
	$K_3Cr(NCS)_6.4H_2O$	476			
	$NH_4Cr(NH_3)_2)NCS)_4$	466			
	$K_2Co(NCS)_4.4H_2O$	475			
	$K_4Ni(NCS)_6.4H_2O$	469			
	$K_2Zn(NCS)_4.4H_2O$	479,470			
	$K_3Rh(SCN)_6$	471,452,438			
	$Tl_3Rh(SCN)_6$	465,428			
	$K_2Pd(SCN)_4$	473,465,439,430			
	$K_2Cd(SCN)_4.2H_2O$	456,458,453,417			
	$K_2Pt(SCN)_6$	454,426,415			
	$K_2Hg(SCN)_4$	451,457,436,431,416			
	$K_3Mo(CNS)_6.4H_2O$	476			
	$(NH_4)_3Mo(CNS)_6.HCl.H_2O$	474			
Tetra(p-chlorophenyl) porphine (12)	Uncomplexed	491	C-Cl stretch	KBr disc	KBr
	V complex	498			
	Cu "	502			
	Co "	503.5			
	Ni "	504.5			
	Zn "	497.5			
Oxalato(13)	$K_2Znox_2.2H_2O$	(a) 519 (b) 428,419 (c) 377,364 (d) 291	(a)ring def. $+CO_2$ bnd (b)MO str.+ ring def. (c)CC str. $+CO_2$ bend (d) ?	mull	CsBr
	$K_2Cuox_2.2H_2O$	481 420 382,370 339			
	$K_2Pdox_2.2H_2O$	469 417 368 350			
	$K_2Ptox_2.2H_2O$	469 405 370 328			
	$K_3Feox_3.3H_2O$	498 366 340 -			
	$K_3Vox_3.3H_2O$	497 368 336 -			
	$K_3Crox_3.3H_2O$	485 415 358 313			
	$K_3Coox_3.3H_2O$	472 446 364 332			
	$K_3Alox_3.3H_2O$	436 485 364 -			
	$Cr(NH_3)_4oxCl$	486,496 366 347 328			
(14)	$Pd(NH_3)_2ox$	374,363,299	none	KBr disc	CsBr
	$K_2[Pdox_2].2H_2O$	374,357			
	$Na_2[Cuox_2(H_2O)_2]$	387,346			
	$Na[Crox_2(H_2O)_2].5H_2O$	398,315			
	$K[Crox_2(H_2O)_2].3H_2O$	399,315			

Class and Reference	Compound	Vibration(cm^{-1})	Assignment	Phase	Cr[illegible]
2-(O-hydroxylphenyl) -imidazoline (16)	Cu^{+2} complex	334	M-N str.	KBr disc	CsBr
	Zn^{+2} complex	374			
	Ni^{+2} complex	336 or 367			
2-(O-hydroxyphenyl) benzimidazole (16)	Cu^{+2} complex	355	M-N str.	KBr disc	CsBr
	Zn^{+2} complex	367			
	Co^{+2} complex	378			
Pyridine (17)	Py	403	ring vibration	mull	KBr
	$MnpyCl_2$	417			
	$MnpyBr_2$	424,419			
	$MnpyI_2$	423,418			
	$Fepy_4(NCS)_2$	426,416			
	$Copy_2Cl_2$	427			
	$Copy_2Br_2$	418			
	$Copy_2I_2$	423,415			
	$Copy_2(NCS)_2$	422,418			
	$Copy_4(NCS)_2$	426,417			
	$Nipy_2Cl_2$	437			
	$Nipy_4(NCS)_2$	440			
	$Nipy_4Br_2$	427			
	$Nipy_4I_2$	430,417			
	$Cupy_2Cl_2$	440			
	$Cupy_2Br_2$	439			
	$Cupy_2(NCS)_2$	416			
	$Cupy_4(BF_4)_2$	433			
	$Agpy_2BF_4$	421			
	$Znpy_2Cl_2$	417			
	$Znpy_2I_2$	420			
	$Znpy_2(NCS)_2$	422,410			
	$Cdpy_2(NCS)_2$	416,413			
	$Cdpy_4(BF_4)_2$	412			
	$Hgpy_2(BF_4)_2$	425			
	$Mnpy_2Cl_2$	417			
	$Copy_2Cl_2$	427			
	$Nipy_2Cl_2$	437			
	$Cupy_2Cl_2$	440			
	$Mnpy_2Cl_2$	422			
	$Cupy_2Br_2$	439			

Class and Reference	Compound	Vibration(cm^{-1})		Assignment	Phase	Optics
Pyridinium Salts (17)	$pyH)_2MnCl_4$	413		none	mull	CsBr
	$pyH)_2CoCl_4$	414				
Unidentate Carbonate (18)	$[Co(NH_3)_5CO_3]Br$	362		Co-O str.	mull	CsBr
	$[Co(ND_3)_5CO_3]Br$	351				
	$[Co(NH_3)_5CO_3]I$	360				
	$[Co(ND_3)_5CO_3]I$	341				
	$[Co(NH_3)_5CO_3]NO_3.{}^1/_2H_2O$	351				
	$[Co(ND_3)_5CO_3]NO_3.{}^1/_2H_2O$	344				
	$[Co(NH_3)_5CO_3]ClO_4$	350				
	$[Co(NH_3)_5CO_3]ClO_4$	338				
Bidentate Carbonate (18)	$[Co(NH_3)_4CO_3]Cl$	(a)	(b)	(a) CoO str.	mull	CsBr
		395	430			
	deuterated	378	418	(b) Co-O-C-O bend		
	$[Co(NH_3)_4CO_3]ClO_4$	392	428			
	deuterated	374	415			
	$[Coen_2CO_3]Br$	353	399			
	deuterated	372	393			
	$[Coen_2CO_3]ClO_4$	362	382			
	deuterated	348	382			
	$KCo(NH_3)_2(CO_3)_2$	366	444,411			
	deuterated	362	438,400			
	$[Co(NH_3)_6][Co(CO_3)_3]$	394,391	488,465			
Ethylenediamine (19)		(a)	(b)			
	$Pten_2^{+2}$	533	?	(a)M-N str.	mull	KBr
	$Rhen_2^{+3}$	580	?	(b)log K_{av}		
	$Coen_3^{+3}$	585	16.3			
	$Pden_2^{+2}$	573	13.5			
	$Cren_3^{+3}$	567	?			
	$Hgen_2^{+2}$	?	11.7			
	$Cuen_2^{+2}$	538	9.8			
	$Nien_3^{+2}$	515	6.0			
	$Coen_3^{+2}$	502	4.6			
	$Znen_3^{+2}$	478	4.0			
	$Cden_3^{+2}$	478	4.0			
(20)		(a)	(b)			
	$[Pten_2]Cl_2$	478(455)	589,546 (509)	(a)ring bend(?)	liq.paraffin	KBr
	$[Pten_2]PtCl_4$	466(445)	583,566 538	(b)MN str.		

Class and Reference	Compound	Vibration(cm^{-1})		Assignment	Phase	Op
			(536,523, 497)	parentheses		
	$[Pten_2Cl_2]$	466(445)	570(516, 508)	denote deuterated bands		
	$[Pden_2]Cl_2$	472(451)	585,521 (534,482)			
	$[Pden_2]PtCl_4$	457	573,545, 506			
	$[Pden_2Cl_2]$	448	561,539			
	$[Cuen_2]PtCl_4$	-	538,525 (463)			
	$[Nien_3]PtCl_4$	-	515,430			
Titanates	$BaTiO_3$	550		TiO_4 octa-hedra vibra-tion	KBrdisc	KBr
Ferrites (23)	$CoFe_2O_4$	374		r_2-a complicated vibration	KBr disc	KRS-5
	$FeFe_2O_4$	370-80				
	$MgFe_2O_4$	406				
	$MnFe_2O_4$	392				
	$NiFe_2O_4$	396				
	$ZnFe_2O_4$	393				
	$Ni_{0.3}Zn_{0.7}Fe_2O_4$	409				
Manganites (24)	$NiMn_2O_4$	465 broad		r_2	KBr disc	KBr
	$CuMn_2O_4$	465 sharp				
Ethylene (25)	$[Pd(C_2H_4)Cl_2]_2$	415 weak		may be M-ethylene	mull	KBr
	$[Pt(C_2H_4)Cl_2]_2$	not investigated				
	$K[Pt(C_2H_4)Cl_3].H_2O$	405 very weak				
	$K[Pt(C_2H_4)Cl_3]$	-				
	trans-$[Pt(C_2H_4)Cl_2(NH_3)]$	-				
1:5 cyclo octadiene (26)	$CuCl.C_8H_{12}$	455		none	?	?
	$PdCl_2.C_8H_{12}$	450				
RuO_4 (27)	RuO_4	330		Ru-O str.	liquid film	CsBr foreprism; grating

Class and Reference	Compound	Vibration (cm^{-1}) (a)	(b)	(c)	Assignment	Phase	Or[illegible]
Nitrito	ONO^-	1335	1250	-	(a)asymm. N-O str.	mull	KBr
Nitro	$K_2Ca[Ni(NO_2)_6]$	1355	1325	30	(b)symm. N-Ostr.		
(28,29)	$K_3[Co(NO_2)_6$	1396,1381	1332	55	(c)a-b		
	$K_2[Pt(NO_2)_4]$	1436,1410 1386	1350	61			
	CH_3NO_2	1582	1384	-			
	$K_3[Co(NO_2)_6]$	413			M-N str.	mull	KBr
	$K_2[Pt(NO_2)_6]$	450					
		(a)	(b)				
	$[Co(NH_3)_6]^{+3}$	502	1		(a)Co-NH_3 str.	mull	KBr
	$[Co(NH_3)_5NO_2]^{+2}$	513,499,488		3	(b)no. predicted bands		
	1,6-$[Co(NH_3)_4(NO_2)_2]^{+1}$	504		1			
	1,2-$[Co(NH_3)_4(NO_2)_2]^{+1}$	511,484,463		4			
	1,2,4-$[Co(NH_3)_3(NO_2)_3]$	514,483,469		3			
	1,2,3-$[Co(NH_3)_2(NO_2)_3]$	481,464	2				
	1,6-$[Co(NH_3)_2(NO_2)_4]^{-1}$	507,438	1				
	$Co(NO_2)_6^{-3}$	-	-				
	$[Co(NH_3)_5NO_2]^{+2}$	499			M-N str.	mull	KBr
	$[Co(NH_3)_5ONO]^{+2}$	?					
	$[Cr(NH_3)_5ONO]^{+2}$	476,466,444					
	$[(NH_3)_3Co\langle{}^{(OH)}_{(OH)}{}_{NO_2}\rangle Co(NH_3)_3]^{+3}$	500					
	$[Cr(NH_3)_6]^{+3}$	455			M-NH_3 str.	mull	KBr
	$[Cr(NH_3)_5Cl]^{+2}$	470,460,431					
	$[Cr(NH_3)_5ONO]^{+2}$	476,466,444					
	$[Cr(NH_3)_5N_3]^{+2}$	448					
	$\beta Cr(NH_3)_5NO_2]^{+2}$	513,499,488					
		(a)	(b)	(c)			
Sandwich Compds.	Cp_2Fe	478	492	170**	(a)antisymm. ring metal str.	mull single crystal	KBr
(30-33)	Cp_2Ni	355	355	125*	(b)antisymm. ring tilt	**reference 100	
	Cp_2Ru	446	528	185*	(c)ring-metal -ring bend	*Calculated	

Class and Reference	Compound	Vibration(cm^{-1})				Assignment	Phase	Cell
		(a)	(b)					
	$(C_6H_6)_2Cr$	456	492			(a)skeletal str.	sublimed	CsBr
	deuterated	421	481			(b)skeletel tilt	film	
Organo Pd and Pt (34)	$(PEt_3)_2Pd$ me Br	510				M-CH_3 str.	KI disc	Grubb Parsons GS2A
	$(PEt_3)_2Pd$ me (SCN)	526						
	$(PEt_3)_2Pd$ me (CN)	502						
	$(PEt_3)_2Pd$ me_2	491,457						
	$(AsEt_3)_2Pdme_2$	498,479						
	$(Pbenz_3)_2Pd$ me_2	529, 482						
	bipy Pd me_2	534, 522						
	cis-$(PEt_3)_2Ptme_2$	523,506						
(35)	cis-$PtCl_2(Pme_3)_2$	689,630				Pt-C str.	mull, solution	?
	cis-$PtCl_2(Pet_3)_2$	643,637						
	trans-$PtCl_2(Pet_3)_2$	632						
		(a)	(b)					
	cis-$Ptme_2(Pme_3)_2$	525,508	678,671			(a)Pt-C str in benzene	-	?
	cis-$Ptet_2(Pme_3)_2$	511,500	678,672					
	cis-$Ptpr_2(Pme_3)_2$	609,601	676,669			(b)Pt-C str. in nujol mull		
	cis-$Ptme_2(Pet_3)_2$	526,506	641,629					
	cis-$Ptet_2(Pet_3)_2$	516,496	-					
	$Ptme_2(Et_2PCH_2CH_2PEt_2)$	521,512	625					
	$Ptme_2(Et_2SCH_2CH_2SEt_2)$	555,548	-					
		(a)	(b)	(c)	(d)			
	trans-$Pt(NO_3)me(PR_3)_2$	567	566	675	630	Pt-C str. (a)R=me benzene (b)R=et benzene (c)R=me nujol (d)R=et nujol	-	?
	trans-$PtClme(PR_3)_2$	551	551	675	630			
	trans-$PtBrme(PR_3)_2$	546	548	675	633			
	trans-$PtIme(PR_3)_2$	538	541	675	633			
	trans-$Pt(NO_2)me(PR_3)_2$	545	544	676	633			
	trans-$Pt(SCN)me(PR_3)_2$	558	556	675	626			
	trans-$Pt(CN)me(PR_3)_2$	-	516	-	637			

Class and reference	Compound	Vibration (cm^{-1})			Assignment	Phase	Optics
		(a)	(b)	(c)	Pt-C str.	-	?
	cis-PtClme $(PR_3)_2$	527	686,675	642,630	(a)R = et		
	trans-PtCl et$(PR_3)_2$	538	-	629	benzene		
	trans-PtIet$(PR_3)_2$	522	-	631	(b)R=me		
	trans-PtClpr$(PR_3)_2$	-	674	-	nujol		
					(c)R=et		
					nujol		
		(a)	(b)		Pt-C str.		
	$PtI_2me_2(PEt_3)_2$	536	540		(a)nujol		
	$PtCl_2me_2(PEt_3)_2$	545,456	-		(b)benzene		
	$PtI_2me_2(Ppr_3)_2$	525,452	-				
(36)							
	cis-$Pt(CH_3)_2(Pme_3)_2$	477,466			Pt-C	benzene	Grubb
	cis-$Pt(CD_3)_2(Pme_3)_2$	522,510			str.		Parsons
	trans-$PtCl(CH_3)(Pme_3)_2$	516					GS2A
	trans-$PtCl(CD_3)(Pme_3)_2$	563					
		(a)	(b)		(a)PtC str.	CCl_4,	Grubb
(37)	trans$(CH_3CO)Pt(PEt_3)_2X$						Parsons
	X = NO_3	541	583		(b)skeletal	mull	GS2A
	NCS	545	583				
	Cl	539	587				
	Br	537	584				
	I	532	580				
	NO_2	554	581				
		(a)	(b)		(a) Pd-C str.	CCl_4,	Grubb
	trans-$(CH_3CO)Pd(PEt_3)_2X$				(b) skeletal	mulls	Parsons
	X = NO_3	521	577				GS2A
	NCS	520	576				
	Cl	515	572				
	Br	513	571				
	I	509	570				
	NO_2	517	575				
		(a)	(b)	(c)	(a)antisymm.	mull	Grubb
Propene					ClPtCl str.		Parsons
(50)	$K[PtCl_3(C_3H_6)].H_2O$	370	330	306	(b)PtCl str.		GS2A
	$K[PtCl_3(C_3D_6].H_2O$	393	330	306	(c)PtCl str.		
					trans to propene		

Class and Reference	Compound	Vibration(cm^{-1})				Assignment	Phase	Cell
		(a)	(b)					
Acetylacetonate (38)	$Coacac_3$	466	2.40			(a) MO str.	KBrdisc	KBr
	$Cracac_3$	459	2.30			(b)force constant		
	$Feacac_3$	434	1.65					
	$Cuacac_3$	455	2.20					
		(a)	(b)	(c)		(a)MO str.	KBr disc	KBr
(39)	$Znacac_2$	422	1.50	8.81		(b)force constant		
	$Coacac_2$	422	1.50	9.51				
	$Niacac_2$	452	2.05	10.38		(c)log $K_{form.}$		
	$Cuacac_2$	455	2.20	14.93				
	$Pdacac_2$	464	2.65	27.1				
(40)	$Niacac_2$	452				MO str.	KBr disc	KBr
	$Niacac_2.py_2$	439						
	$VOacac_2$	480						
	$VOacac_2.py_2$	463						
(41)	$Alacac_3$	400				No assignments but metal sensitive	mull	CsBr
	$Cracac_3$	360						
	$Mnacac_3$	339						
	$Feacac_3$	301						
Ammines (42)	$Co(NH_3)_6Cl_2$	318				Co-N str.	mull, KBr disc	CsBr
	$Co(NH_3)_6Br_2$	317						
	$Co(NH_3)_6I_2$	308						
	$Co(NH_3)_6Cl_3$	328						
	$Co(NH_3)_6Br_3$	322						
	$Co(NH_3)_6I_3$	320						
	$Hg(NH_3)_2Cl_2$	513				Hg-N str.	mull, KBrdisc	CsBr
	$Hg(NH_3)_2Br_2$	499						
		(a)	(b)			(a)Co-N str.	mull, KBr disc	CsBr fore-prism grating
(43)	$Co(NH_3)_6Br_3$	464	325			(b)NCoN def.		
	$Co(NH_3)_6I_3$	464	318					
		(a)	(b)	(c)	(d)			
	trans-$[Co(NH_3)_4Cl_2]Cl$	501	463	353	290	(a)antisym CoXstr.	same	same
	trans-$[Co(NH_3)_4Br_2]Br$	486	465	318	294	(b)CoNstr (c)NCoX def. (d)NCoN def.		

Class and Reference	Compound	Vibration (cm^{-1}) (a)	(b)	(c)	Assignment	Phase	Opposite
	$[Co(NH_3)_5F]Br_2$	504,493	449	310	(a)antiphase	same	same
	$[Co(NH_3)_5Cl]Br_2$	487,479	457	325,283	CoX+CoN		
	$[Co(NH_3)_5Cl](NO_3)_2$	487	462	323,283	(b) CoN str.		
	$[Co(NH_3)_5Br]Cl_2$	487	462	324	(c) NCoN		
	$[Co(NH_3)_5I]Br_2$	428	473	319	def. and NCoX def.		
(44)	trans-$Pt(NH_3)_2Cl_2$	326			MN str.	KBr disc	CsBr
	deuterated	332					
	cis-$Pt(NH_3)_2Cl_2$	322					
	deuterated	322					
	trans-$Pt(NH_3)_2Cl_4$	300					
	$Cu(NH_3)_2Cl_2$	481,306					
	$Hg(NH_3)_2Cl_2$	471					
	$Zn(NH_3)_2Cl_2$	442,306					
	$Cd(NH_3)_2Cl_2$	374					
	$Pt(NH_3)_4Cl_2.H_2O$	497					
	$Zn(NH_3)_4I_2$	410					
	$Cu(NH_3)_4Cl_2$	420					
	$Cd(NH_3)_4Cl_2$	381					
	$Hg(NH_3)_4(ClO_4)_2$	408					
(45-47)	trans-$Pt(NH_3)_2Cl_2$	507			MN str.	mull	KBr
	cis-$Pt(NH_3)_2Cl_2$	508					
	cis-$Pt(NH_3)_2(NO_2)Cl$	510					
	trans-$Pt(Et_2S)Cl_2(NH_3)$	493					
	trans-$Pt(C_2H_4)(NH_3)Cl_2$	481					
	cis-$Pd(NH_3)_2Cl_2$	477,497					
	$[Co(NH_3)_5Cl]Cl_2$	493					
	deuterated	487					
	trans-$Pd(NH_3)_2Cl_2$	496					
	deuterated	493					
	cis-$Pd(NH_3)_2(NO_2)_2$	496,463					
	$Pd(NH_3)_4Cl.H_2O$	498					
	$[Co(NH_3)_6]Cl_3$	502					
	$Pt(NH_3)_4Cl_2$	511					
(48)	$HgNH_2Br$ cubic	510			HgN str.	KBrdisc	CsBr
	$HgNH_2Br$ rhombic	560					

Class and Reference	Compound	Vibration (cm^{-1}) (a)	(b)	Assignment	Phase	Optics
Carbonyls (51,52)	$Ni(CO)_4$	422	459	(a)NiC str. (b)NiCO bend	Vapor	CsBr

	Reference	Bands Found	Assignment	Phase	Optics	Structure	Comments
$Fe(CO)_5$	(53)	472 522	CO bend -	gas,liquid	KBr	trig.bipy.	No 377 364 475
	(54)	93 72	- -	?	?	?	No 377 364
	(55)	364 377 430 475	apical FeC str. Fe-C str. in phase FeCO bend out of phase FeCO bend	gas	KBr	tetr.bipy.	364,377 crucial to structure
	(56)	364 377 430 472	Comb. eq FeC str. eq CO bned ax FeC str.	evaluates old data		trig.bipy.	
	(57)	68 * 114 104 *	γ_9 γ_{14} γ_{15}	vapor	grating	trig.bipy.	* = calc. from comb.
	(57)	93 72	γ_{15} γ_9	liquid	grating	trig.bipy.	
$Fe_3(CO)_{12}$	(58)	575 594	C-Fe stretches	solution	CsBr	?	
$Co_2(CO)_8$	(59)	531 641	Co-C-bend Co-C str.	solution	?	2 bridge carbonyls Co-Co bond	
$Cr(CO)_6$	(60)	436 661	CrC str. CO wag	gas	KRS-5	octahedral	
	(57)	98	CCrC bend	gas	grating	octahedral	

	Reference	Bands Found	Assignment	Phase	Optics	Structure	Comments
$Mo(CO)_6$	(60)	368	MoC str.	gas	KRS-5	Octahedral	
		595	CO wag				
	(57)	81	CMoC band	gas	grating	Octahedral	
	(61)	agrees with others	-	Solid, gas	CsBr	Octahedral	
$Mn_2(CO)_{10}$	(62)	625	none	solid, solution	?	biocta-hedral (X-ray)	with M-M bond
$Re_2(CO)_{10}$	(62)	455	none	same	?	same	
Carbonyl Hydrides	(59)	548	CoCO bend	solution	?	basically tetrahedral	
		704	CoC str.				
$HCo(CO)_4$	(63)	330	sym. CoCstr.	gas	CsBr	basically tetrahedral	
		403	CoC str. + CoCO bend				
		467	Co bend				
		541	Co bend				
		703	CoC str.				
	(65)	1934	Co-H str.	gas	?	basically tetrahedral	
		1400	2(CoC str.)				
$DCo(CO)_4$	(64)	600	Co-C str.	gas	CsBr	proves that O partici-pate	C and/or with H or D.
		296	sym. CoC str.				
	(65)	1396	Co-D str.	gas	?		
		1193	2(Co-C str.)				
$HMn(CO)_5$	(64)	615	MnH bend + CO bend	?	?	?	
		664	CO bend				
		735	MnH bend + CO bend				
		458	none				
		1782	Mn-H str.				

	Reference	Bands Found	Assignment	Phase	Optics	Structure	Comments
$DMn(CO)_5$	(64)	676 doublet 1287	CO bend + CO bend MnD str.	?	?	?	
$[Co(CO)_4]^-$	(59)	555 1833	CoCo bend CO str.	pyridine	?	tetrahedral	
	(67)	530	none	THF	CsBr	-	
$Mn(CO)_5^-$	(67)	467 511 564	none	THF	CsBr	-	
$Co(CO)_3NO$	(68)	390 442 467 483 528 565	CoC symm str. deg. CO bend CO bend symm. CO bend CoN symm str. CoC asymm. str.	gas	CsBr	tetrahedral	diffraction agrees
	(69)	confirms above	-	-	-	tetrahedral	

Class and Reference	Compound	Vibration (cm^{-1})			Assignment	Phase	Optics
carbonyl-amine (70)	trans-$Pt(CO)(p\text{-}tol)Cl_2$ trans-$Pt(CO)(p\text{-}tol)Br_2$ trans-$Pt(CO)(p\text{-}tol)I_2$ trans-$Pt(CO)(an)Br_2$ trans-$Pt(CO)(an)I_2$ trans-$Pt(Et_2S)(NH_3)Cl_2$ trans-$Pt(NH_3)_2Cl_2$	488 492 493 481 482 493 507			Pt-N str.	mull	CsBr
Cyanide Complexes (75)	$Ni(CN)_4^=$	(a) 543	(b) 448	(c) 430	(a)NiC str. (b)out plane NiCN bend (c)inplane NiCN bend	KBr dics, mull, single crystal	CsBr
(76)	$K_3Cu(CN)_4$	(a) 304	(b) 306		(a)CuC str. (b)CuCN bend	single crystal	CsBr

Class and Reference	Compound	Vibration(cm^{-1})			Assignment	Phase	Optics
		(a)	(b)		(a)CN wag		
(77)	$Pt(CN)_4^{=}$	300	505		(b)PtC str.	KBr disc	CsBr
		(a)	(b)		(a) M-C str.		
(78)	$Fe(CN)_6^{-3}$	505	2125		(b)CN str.	?	?
	$Fe(CN)_6^{-4}$	584	2047				
	$Cr(CN)_6^{-3}$	462	2127				
	$Mn(CN)_6^{-3}$	514	2125				
	$Mn(CN)_6^{-4}$	-	2060				
	$Mn(CN)_6^{-5}$	-	2043				
(71-73)	$[Ag(CN)_2]^-$	390			M-C str.	mull	CsBr
	$[Au(CN)_2]^-$	427					
	$[Hg(CN)_2]^-$	442					
(74)	$K_2Zn(CN)_4$	358	315		both MC str.	mull,	CsBr
	$K_2Cd(CN)_4$	316	-		+ NCM bend	crystal	
	$K_2Hg(CN)_4$	330	-				
(79)	$Co(CN)_6^{-3}$	422			M-C str.	?	?
	$Cr(CN)_6^{-3}$	457					
	$Mn(CN)_6^{-3}$	443					
	$Fe(CN)_6^{-3}$	416					
(80)	$K_3Co(CN)_6$	416			CoCN bend	single	CsBr
		564			CoC str.	crystal	
		(a)	(b)		(a)MC str.		
(81)	$K_3[Co(CN)_6].3H_2O$	565	414		(b)MCN bend	mull,	CsBr
	$K_4[Fe(CN)_6].3H_2O$	585	414			KBr disc	fore-
	$K_3[Fe(CN)_6].3H_2O$	511	387				prism,
	$K_4[Ru(CN)_6].3H_2O$	550	376				grating
	$K_4[Os(CN)_6].3H_2O$	554	360				
		(a)	(b)	(c)	(a)MC str.		
	$[Co(NH_3)_6][Co(CN)_6]$	562	328	455	(b)NCoN def.	same	same
	$[Co(NH_3)_6][Fe(CN)_6)]$	511	330	459	(c)MCN bend		

Class and Reference	Compound	Vibration (cm^{-1})	Assignment	Phase	Optics
(82)	$K_4Mo(CN)_8.2H_2O$	402	none	KBr	CsBr
	dehydrated	388		disc	
	$K_3Mo(CN)_8.2H_2O$	402			
	dehydrated	388			
	$K_4W(CN)_8.2H_2O$	407			
	dehydrated	400			
	$K_3W(CN)_8.2H_2O$	407			
	dehydrated	400			

References 83-99 contain material on halo compounds of transition metals. The material is omitted due to space limitations.

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A MASS-SPECTROMETRIC STUDY OF SULFUR VAPOR from 81°C to 1,737°C.*

J. R. Marquart October 25, 1962

INTRODUCTION

Although a number of experiments have been performed in order to ascertain the composition of sulfur vapor, there has been a great deal of disagreement as to interpretation of results. Vapor-density measurements were made as early as 1909(1) and again in 1941(2). In both instances, the data were explained on the basis of only S_8, S_6, and S_2 species being present. More recent work by Braune, Peter and Neveling(3) indicated that S_4 must be included in the species. This conclusion has received support from optical absorption studies(4). Knudsen cell effusion studies (5,6,7) showed that S_8 is predominate at all temperatures up to the melting point. Fouretier(8), measuring the pressure exerted on a piston, and Taillade(9), incorporating entrainment in a carrier gas, obtained vapor-pressure values somewhat larger than those found by the Knudsen experiments, but the interpretation remained unchanged. West and Menzies(10), in a careful experiment, measured the total vapor pressure above liquid sulfur by a static isoteniscope. Their data agreed well with the determination of the sulfur point (11).

Guthrie, et. al.,(12) calculated the thermodynamic properties of S_8 gas and found that $\underline{K}$ eq for the reaction $4S_2(g) \rightleftarrows S_8(g)$, as calculated from the $\Delta H°$ and $\Delta S°$ values, disagreed with that calculated directly from vapor composition results (1,3). They concluded that other vapor species than S_8, S_6, S_4, and S_2 are present.

Three mass-spectrometric studies of sulfur (13,14,16) have shown that S_2 predominates over all other species, whereas a fourth study(15) has indicated that only S_8, S_7, S_6, and S_5 are primaries in the vapor.

Predissociation in the emission spectrum of sulfur sets the upper limit for the dissociation energy of diatomic sulfur at 4.4-ev. However, 3.6 and 3.3 are also possible values depending upon the state of excitation of atomic sulfur(17). Gaydon(17) accepted the predissociation limit as the probable value of the dissociation energy, whereas Herzberg and Mundie(18) preferred the 3.6-ev value. Various experiments have given support to each of these values: 3.3ev. (19,20,21), 3.6 ev. (22,23,24,14), and 4.4 ev. (25,26,27,28,29,30,31).

* Work performed by J. R. Marquart and J. Berkowitz at Argonne National Laboratory, Argonne, Illinois

Large discrepancies have also occurred in the values of appearance potentials, particularly for S_2^+. These range from about 10.7 ev (32,33) to about 8.3 ev (13).

Therefore, a study was under taken at this laboratory to attempt to resolve the uncertainty arising in the composition and thermodynamic properties of sulfur vapor. It was decided to extend the temperature range of mass-spectrometric studies by observing the vapor composition of a number of metal sulfides which decompose to sulfur upon heating, as well as by vaporizing rhombic sulfur itself.

EXPERIMENTAL ARRANGEMENT

The arrangement of the Knudsen cell and ion source was virtually identical to that described by Berkowitz and Chupka (34). A study was made to determine materials for use as a Knudsen cell which remain inert to each specific sulfide. It was found that platinum was satisfactory for ZnS and Cd S; fused-alumina lined molybdenum for S, Na_2S_2, Sb_2S_3, FeS, and HgS; and molybdenum for CaS and SrS. Temperature of the Knudsen cell was determined by a Pt, Pt-10%Rh thermocouple for temperatures up to 1000°C and by an optical pyrometer for higher temperatures.

EXPERIMENTAL RESULTS

In each experiment, it was found that the major ion peaks could be identified as due to multiples of sulfur and in a few instances to the ions of the metal or metal sulfide. The experimental results are summarized in Tables I through IV.

DISCUSSION

On the basis of the extrapolated vapor composition obtained in Table IV, it appears that at 400°K. and about 6.56×10^{-5} atmospheres pressure S_8 is the predominate species whereas S_6 and S_7 are also significant. The value of the appearance potential for S_2^+ is only about 0.7 ev higher for the sulfur experiment than for the higher temperature experiments, but the source of S_2^+ appears to be fragmentation of higher polymers in the electron beam. Furthermore, contrary to the results of other experimentors (13,14,16), S_2^+ was not found to be the predominate species. It should be noted, however, that Hagemann (16) reports that his data were taken by a double oven arrangement with the source at 523°K. and 10^{-5} mm. pressure. If this was the case, then the added tendency toward lower polymers at higher temperature and lower pressure makes his data agree with this experiment.

The enthalpy of dissociation of each polymer was calculated from the slope of the log $\underline{K}$ eq $\underline{vs.}$ 1/T plot for the reaction and also, where entropy data are available, from the $\Delta F°$ of the reaction which was based on the equilibrium concentration of

Table III. It is noted that enthalpies determined by the second method are higher by one to two kcal. for the S_8, S_6, and S_4 reactions. But it should be remembered that the literature values of the entropies are somewhat doubtful. The dissociation energy for S_2 appears to be about 107.16 kcal., which lends support to the spectroscopically proposed values of 4.4 ev. or 101 kcal.

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Table I. Appearance Potentials[a] (electron volts) of Sulfur and Sulfide Vapor

Ion \ Sample and Temp.	Sulfur 383°K	HgS 507°K	Na_2S_2 814°K	CdS 953°K	ZnS 1116°K	FeS 1388°K	SrS 1934°K	CaS 1962°K.
S^+ (mass 32)	17.7±.5	13.7±.5	14.2±.5	14.7±.5	14.0±.2	11.5±1.0	10.357[b]	10.357[a]
S_2^+ (mass 64)	10.2±.5	9.7±.5	9.6±.5	9.5±.5	9.6±.4	8.5±1.0	9.31±.2[b]	9.45±.2[b]
S_3^+ (mass 96)	13.5±.5	10.7±.5	10.5±.5	10.0±.5				
S_4^+ (mass 128)	13.5±.5	10.7±.5						
S_5^+ (mass 160)	10.0±.5	9.7±.5						
S_6^+ (mass 192)	9.5±.5	9.5±.5						
S_7^+ (mass 224)	9.5±.5	9.7±.5						
S_8^+ (mass (256)	9.0±.5	9.7±.5						
M^+ (metal ion)			8.0±1.0	8.5±.5	9.6±.4		5.4±.5	5.9±.4
MS^+ (metal sulfide ion)							5.7±.5	6.4±.4

(a) All appearance potentials normalized by comparison to appearance potential of Hg^+ as 10.43 except (b).

(b) Normalized relative to appearance potential of S^+ as 10.357.[b]

Table II. Estimated Partial Pressures of Sulfides[a] (atm)

Species \ Sample and Temp	HgS 480°K	Na_2S_2 814°K	CdS 986°K	ZnS 1203°K	FeS 1318°K	SrS 1809°K	CaS 1972°K
S						2.56×10^{-7}	5.61×10^{-6}
S_2	9.03×10^{-8}	1.08×10^{-5}	2.21×10^{-5}	3.24×10^{-5}	1.22×10^{-5}	4.91×10^{-8}	1.24×10^{-6}
S_3	3.43×10^{-9}	1.34×10^{-8}	8.61×10^{-9}	6.08×10^{-9}			
S_4	4.38×10^{-9}	3.45×10^{-9}	3.46×10^{-10}				
S_5	3.66×10^{-9}						
S_6	1.64×10^{-8}						
S_7	1.56×10^{-9}						
S_8	1.96×10^{-9}						
M(metal)	2.68×10^{-8}	9.97×10^{-9}	1.31×10^{-5}	2.30×10^{-5}	$<5.9\times10^{-15}$	1.33×10^{-7}	2.17×10^{-5}
MS(metal sulfide)	1.2×10^{-9}	4.27×10^{-10}	$<9.6\times10^{-9}$	$<1.5\times10^{-10}$	$<2.8\times10^{-15}$	1.03×10^{-9}	2.25×10^{-8}
Total	1.50×10^{-7}	1.10×10^{-5}	3.55×10^{-5}	5.58×10^{-5}	1.22×10^{-5}	4.39×10^{-7}	7.85×10^{-5}

(a) All partial pressures estimated by applying the constant 3.0299×10^{-12} atm/unit grid intensity deg. obtained for S_2 by evaporating a known amount of ZnS to dryness whil continually monitoring mass 64. All other species were corrected for ionization cross-section on the basis of 1 for S, 1.5 for S_2, 2.0 for S_3, 2.5 for S_4 --- 4.5 for S_4 estimated on the basis of the results of Berkowitz, Tasman, and Chupka, J. Chem. Phys., (in Press) and using Otvos and Stevensons ratios (41) for the metal and metal sulfide.

Table III

RELATIVE ION INTENSITY AND COMPOSITION OF SULFUR VAPOR

Species	Relative Ion Intensity 375°K.	Estimated Partial Pres. 400°K	% 400°K
S	9.22	2.05×10^{-30} atm.	3.1×10^{-24}
S_2	75.32	4.74×10^{-8}	7.2×10^{-2}
S_3	17.08	1.79×10^{-8}	2.7×10^{-2}
S_4	38.37	7.09×10^{-8}	1.08×10^{-1}
S_5	32.82	3.04×10^{-7}	4.63×10^{-1}
S_6	27.82	1.02×10^{-5}	15.48
S_7	3.69	3.12×10^{-6}	4.76
S_8	100	5.19×10^{-5}	79.09

TABLE IV. THERMODYNAMIC FUNCTIONS FOR DISSOCIATION OF SULFUR VAPOR SPECIES

gas reaction	These data ΔH°_{400} kcal (a)	Keq units of atm. (b)	ΔF°_{400} kcal	ΔS°_{400} cal/deg. (c)	Braune et al (3) Literature ΔH° kcal	$\Delta H^\circ_{623-1273}$ kcal	Calc from this data and Literature ΔS°_{400} cal/deg.	ΔF°_{400} kcal
1/4 $S_8 \rightarrow S_2$	19.89	5.58×10^{-7}	11.44	21.13	22.57 (d)(e)	23.05	25.75 (e)	21.74
2/7 $S_7 \rightarrow S_2$	17.63	1.77×10^{-6}	10.53	17.75				
1/3 $S_6 \rightarrow S_2$	17.22	2.19×10^{-6}	10.36	17.15		21.25	22.43 (f)	19.33
2/5 $S_5 \rightarrow S_2$	14.63	1.92×10^{-5}	8.63	15.00				
1/2 $S_4 \rightarrow S_2$	13.07	1.78×10^{-4}	6.86	15.53		14.20	18.55 (f)	14.28
2/3 $S_3 \rightarrow S_2$	10.23	6.92×10^{-3}	3.95	15.70				
1/2 $S_2 \rightarrow S$	54.64	9.42×10^{-27}	47.63	17.52	53.58 (d)		13.31 (f)	52.95

(a) From slope of log Keq vs 1/T Plots.
(b) From Partial Pressures of Table III.
(c) Calculated from H°_{400} and F°_{400}.

Thermodynamic functions used in cal:
(d) Evans and Wagman[39] : S°_{400} for S(g) = 41.7358, S°_{400} for S_2(g) = 56.85, $H^\circ_{400}-H^\circ_0$ for S(g) = 2162.5, $H^\circ_{400}-H^\circ_0$ for S_2(g) = 2952.
(e) Guthrie et al[12]: $H^\circ_{400} - H^\circ_0$ for S_8(g) = 11,480.
(f) Interpolated from Luft[40].

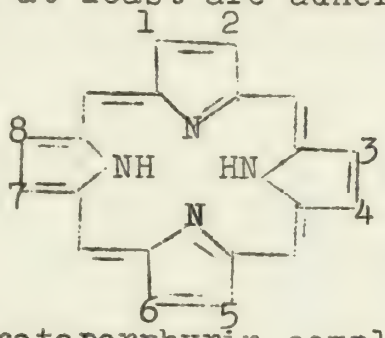
STUDIES OF THE HAEMOPROTEINS

B. W. Baylis October 30, 1962

INTRODUCTION

Perhaps the most useful introduction to this material, as presented to inorganic chemists, would be an explanation of terms. Therefore, there follow definitions, which, even if not entirely generally accepted, at least are adhered to in this paper.

Phosphine



Derivatives of phosphine found naturally are indicated on Table I on page 54.

Haem group: protoporphyrin complex of iron (II).
Haemochrome: haem with variable donor molecules above and below the plane of the ring.
Haemoglobin: haem with its specific protein attached at one end of the z axis and usually with water at the other. This often refers to that naturally occurring material which has four sub-units of this type.
Haemoprotein: the group of naturally occurring iron(II) or iron(III) complexes with various porphyrins and various donor molecules.
Donor molecule is used here only for molecules or ions along the z axis.
Substituent is used here to refer only to side chains on the porphyrins or model chelating groups.
Methaemoglobin: haemoglobin the iron of which is oxidized to +3.

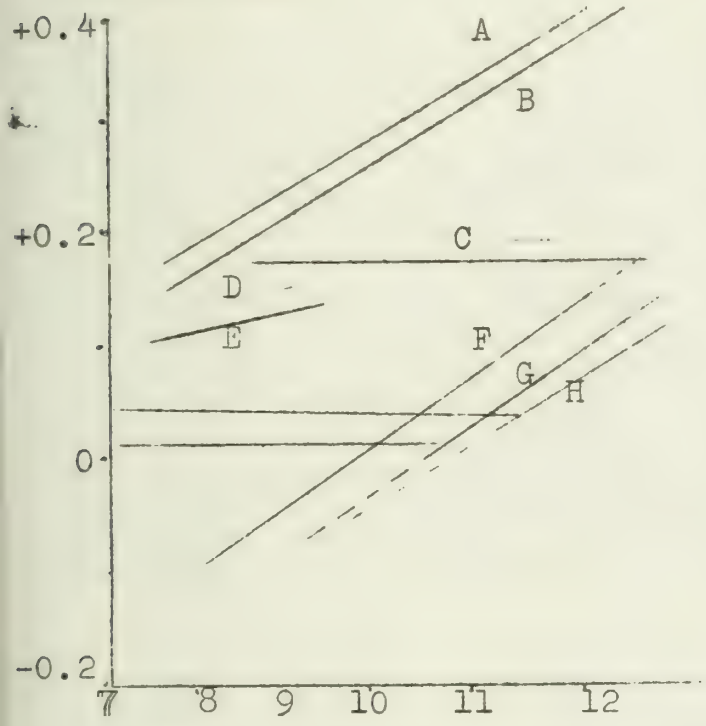
Attention should be drawn to the seminar given last fall (1) on the metalloporphyrins. None, or at least very little, of the material covered in that seminar is mentioned here.

OXIDATION-REDUCTION POTENTIAL STUDIES

Studying the oxidation potential of iron in haemoproteins has proved quite complicated. These systems display poor reversibilities and worse solubility properties. In addition, the potentials vary with pH, steric and electronic requirements of both substituents on the porphyrin and ligands at the 1:6 sites of the iron, and spin states of the iron(II) and iron(III). Of course these variables are all interconnected. The experiments in this area represent an attempt to sort out each set of variables and examine it alone. When this was not done, the interpretation of the data was subject to considerable error by oversimplification.

In addition to the experimental difficulties involved, the use of the naturally occurring haemoproteins brings in too many unknown factors for an interpretation to be possible. Hence model systems are devised and studied and the results compared with results of similar studies on the naturally occurring materials. If the two sets of results bear enough resemblance, or if major differences can be rationalized, the interpretation developed from the model system is used to make understandable the data on the natural system.

Martell and Calvin(2) report the following data showing the variation of oxidation potential with pH for several haemochromes.



A: haem in borate buffer
B: haem in phosphate buffer
C: dicyanohaem
D: dipilocarpinehaem
E: dihistidinehaem
F: di picolinehaem
G: dipyridinehaem
H: dinicotinehaem

Lines A,B,F,G, and H indicate that these derivatives change with pH in a way that stabilizes the iron(III). It is doubtful that the second amine remains in the coordination sphere. This hypothesis allows for the following explanation:

$$Fe^{II}PN_2 - e^- \rightarrow Fe^{III}PN_2 \xrightarrow{OH^-} Fe^{III}PN(OH) + N$$

An anionic ligand can stabilize a higher oxidation state; thus the hydroxide will stabilize the iron(III). Calculation of the variation of the observed $\underline{E}°$ with $\underline{p}H$ based on this equilibrium gives a curve with a slope of 0.60. This is noted to be the slope observed for lines A,B,F,G and H. The iron-cyanide bond is too strong to be affected by the hydroxide ion. Hence, there is no variation in $\underline{E}°$ with $\underline{p}H$ for line C. The slopes of lines D and E are explained by a proposed removal of less than one hydrogen ion per iron. This could be accomplished either by removing a hydrogen ion from some of the imidazole rings or by displacing some of the rings by hydroxyl ions.

Changing the substituents on the pyrrole rings changes the potential. R. J. P. Williams (3), using 8-hydroxy quinoline-iron complexes as his models, studied the effects on E° of change in pH while varying the substituents. Comparison of E_f with acid constants of the ligands led to no simple relationship. With the 5-cyano and 5-formyl derivatives anomalously low poteneials were obtained, indicating stabilization of the iron(II). These substituents are π acceptors, a fact which is not reflected in the pKa of the ligand. The increased π acceptance of the ligand will stabilize the iron(II), which is 10-30% diamagnetic.

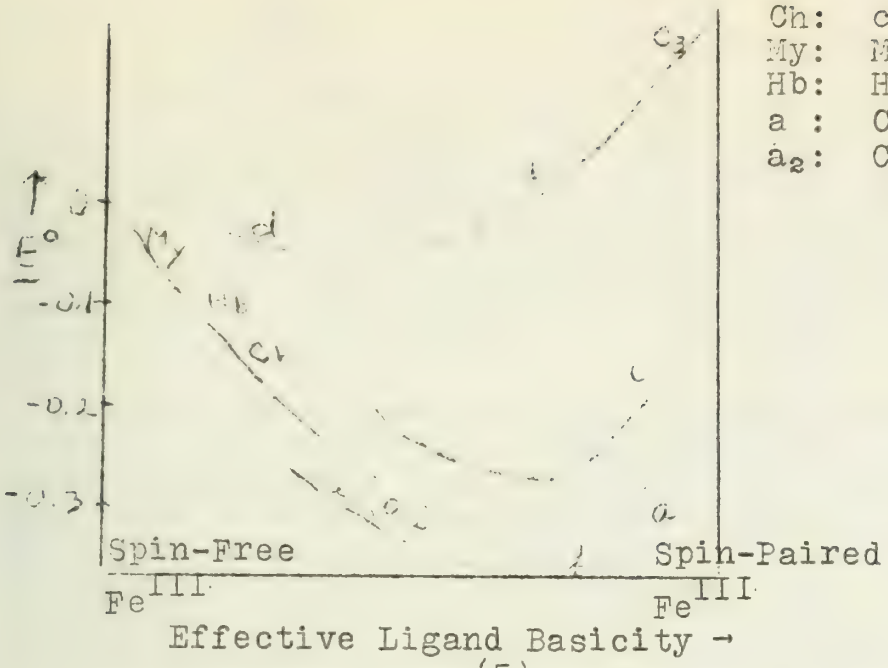
The oxidation potentials of derivatives of the 1,10-phenanthroline complexes(3) are all about -1 volt, indicating stabilization of the iron(II). The reduced form is diamagnetic, and the oxidized form is a mixture of spin-paired and spin-free complexes. The reagent 2-methyl phenanthroline provides an exception, with an oxidation potential of 0.585 volt. Its iron(II) complex is paramagnetic, indicating that the ligand cannot interact as strongly with the metal as before. This may be caused by steric interference by the methyl group. These studies refute the earlier assumption (2) that the stability of iron(III) complexes, and hence the oxidation potential, is increased by increasing electron-donor properties of the substituents. It was here shown that this is only true if both oxidation states are either spin-free or spin-paired. In any case, iron(II) is always stabilized by electron acceptance. The biologically important complexes contain diamagnetic iron(II) and spin-free or a mixture of spin-free and spin-paired iron(III). Therefore, in these σ donors and π acceptors will stabilize the iron(II).

Williams (4) has recently studied iron-dipyridyl complexes as a model system. Comparing E_f with pKa values of the substituted ligands indicates that the variation in oxidation potential is dominated by the spin state. This information can be applied to explain the data available on porphyrins. Other pertinent information follows:

1) The iron(II)-nitrogen distance is 0.1-0.2 Å. longer than the iron(III)-nitrogen distance. Therefore, steric considerations are of greater importance in spin-paired iron(III) complexes.

2) Sigma donor power of the nitrogen atoms in the porphyrins decreases in the order meso or haemato > proto > rhodo > dihydro. These porphyrins are described in the Table on page 54.

3) Pi acceptor power of the porphyrins decreases in the order rhodo > proto > meso or haemato > dihydro.



The observed chart(5) could result from reduced steric restrictions around the iron and a change from imidazole to primary amine ligands as one proceeds from left to right. Properties of the porphyrins prove less important. Considerations of this type have led to the assignments of many of the donor groups listed on the Table on page 54.

Williams (6) gives the order of increasing oxidation potential of iron(II)- dimethyl glyoxime base$_2$ as pyridine < imidazole < water < ammonia < hydroxide. Falk(7) summarizes the considerations involved in the change in oxidation potential with change in donor molecule as follows:

1) Electrostatic forces. If the donor is an anion, the higher valence state will be favored, raising the potential.

2) Back-double-bonding. This favors the lower oxidation state, lowering the potential.

3) Ligand-field stabilization energy. This varies with the cations and spin states involved.

4) The pKa values of the ligands. In a series of related ligands, increasing pKa causes an increase in oxidation potential.

It is worth noting that the curves of E° versus pH and the log of oxygen absorption by haemoglobin are quite similar. From this Martell and Calvin(2) conclude that the processes involved are similarly affected by changes made on the molecule. The oxidation potential of haemoglobin at the pH if blood is -0.1 volt. Thus the effect of the donor groups is to decrease the tendency towards oxidation but not so much as to prevent oxygenation. Oxygen further stabilizes the spin-paired complex.

SPECTRAL STUDIES

Spectra have been studied for haemoglobin over the IR, visible, and UV regions (8). Most important are the α and β bands, the Soret or γ band, and the charge-transfer bands. The first three are considered to be $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions by some(9). Platt(10) has carried out molecular-orbital calculations to arrive at expressions for the energy states of the porphine molecule. The lowest energy transitions possible correspond to the α and β bands.

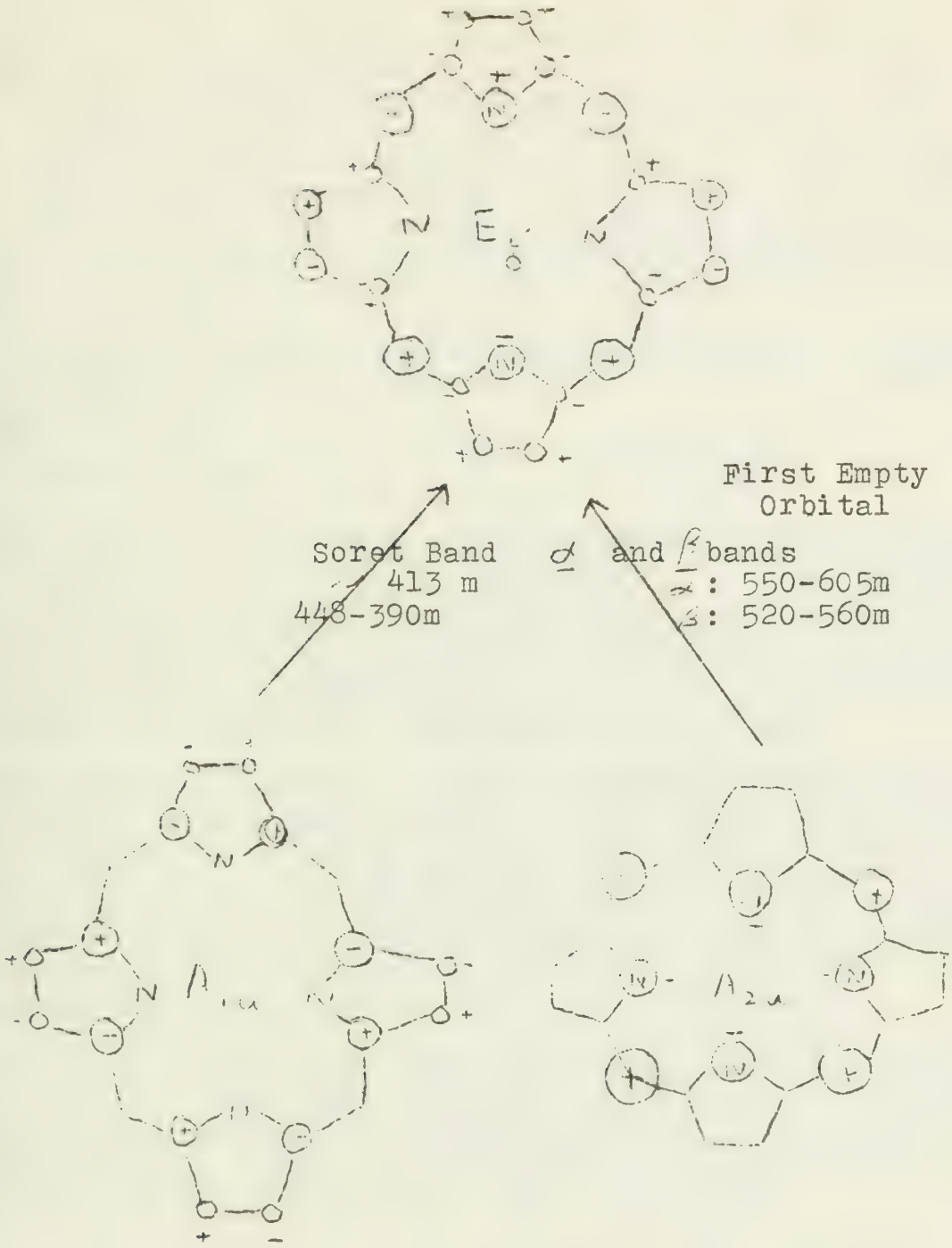
In porphine there are four of the longer wavelength bands, I,II,III, and IV(9,10). Bands III and IV arise from transitions involving electron density moving away from the amine hydrogens, and I and II arise from electron density moving away from the nitrogens that are not bound to a hydrogen. Bands I and III do not involve any change in vibrational state(10). Bands II and IV arise from coupling of the electronic transition with a change in vibrational state. Hence I and III are strengthened by substituents increasing the asymmetry, whereas II and IV do not change. This behavior has also been observed for the α and β bands of the metal porphyrins. Therefore I and III seem related to the α and II and IV to the β bands.

Upon inserting several divalent cations, Williams (9) observed that the wavelengths for α and β decreased with increasing electronegativity of the cation. The greater the ability of the cation to donate π density, the greater the decrease in the wavelengths of α and β.

Haem is paramagnetic and its γ band is weak and appears around 575 mμ. After accepting either pyridine or ammonia the complex becomes diamagnetic, α shifts to 538 mμ, and its intensity increases markedly. Additional ligands change the haemchrome only slightly. Oxygen, carbon monoxide, cyanide, etc., do change the magnetic moment, increase the intensity of γ and move α and β to shorter wavelengths. The shift of α and β to lower wavelength is less with neutral bases than with anions(6). In general, α, β, and γ bands do not move far unless there occurs a change in the spin state. The wavelength of γ goes up with a change from spin-free to spin-paired in iron(III), but it goes down with iron(II) complexes (5). Although $\Delta\lambda$ (λ_{Fe}II-λ_{Fe}III) indicates a spin free complex in spin-paired cases, the wavelength of α and β are longer the stronger the donor character of the ligand. If the donor molecule is a double-bonding ligand, the more electron-attracting the substituents on the porphyrin, the greater the shift to longer wavelength of the α and β bands(7).

The intensity of the Soret band does not vary unless attack occurs on the porphyrin ring(6). The α and β bands are more intense with low than with high spin complexes. The intensity of α varies with substituents, but β remains constant. The intensity ratio of α to β increases with increasing π donation

ELECTRONIC TRANSITIONS



GROUND STATE

character of the donor molecule. Reasons for the variance of intensity and position of the γ and β bands as the substituents are changed are given by Gouterman(11).

Many spin-free iron(III) complexes with unsaturated anions have absorbance bands between 600 and 650 mμ and 450 and 500 mμ (6). These are also present in methaemochromes. Because charge transfer involves a change in dipole moment these bands are intense. Low-spin methaemochromes give no charge-transfer bands. The charge-transfer bands move to shorter wavelength as σ donation of the donor molecules increase. Unsaturated ligands raise the wavelength more than their σ donation ability would indicate. Obviously π interaction is involved here.

In spectra of spin-paired haemoproteins there is a band at 500 mμ. This is also in iron(II) complexes of unsaturated nitrogen bases (9).

OTHER PHYSICAL METHODS

Orgel(12) used electron spin resonance to study hydroxy haemoglobin. His data indicate anisotropy even in the xy plane. This might be caused by approach of the π cloud of the imidazole group. This would be in a position to interact with one of the degenerate d_{xz} and d_{yz} orbitals but not the other. He found the differences in energy to be 800 cm.$^{-1}$ between d_{xy} and d_{xz} and the same splitting between the d_{xz} and d_{yz}.

X-ray methods have been used to study the structure of myoglobin and haemoglobin. The structure of myoglobin has been determined to 2 Å (13). This shows an imidazole residue pointing down the z axis of the haem group. The rest of the protein is wound around, affording a hydrogen bond site for a carboxylic acid group of the porphyrin. In addition, there is a second imidazole residue pointing up the z axis, but it is far enough away to be only mildly affected by the iron.

The haemoglobin study has been completed to a resolution of 5.5 Å. (14). This shows that each of the four units is quite similar to the myoglobin. It also gives an orientation for the four haem groups. These studies indicate that the four units are really similar pairs of 2 identical units.

Orientation of the Haem Groups

Since the protein is attached to a side chain on the porphyrin, asymmetry about each iron is possible. The optical rotary dispersion of catalase(15) indicates that the group of four units exhibits dispersion at 600 mμ but there is no Cotton effect from the single units.

CHEMICAL STUDIES

Hydrolysis studies of these compounds have proved enlightening(6). Complexes with zero or negative charge are difficult to hydrolyze. Thus the pH necessary increases with greater negative charge on the complex. Peroxidase, methaemoglobin, and metmyoglobin hydrolyze at similar pH, indicating similar negative charge. Catalase requires strong base, indicating that the donor molecules are two carboxylates.

Oxygen appears to be absorbed only if there are no active hydrogens on an atom bound to the iron(6). Haemoglobin absorbs oxygen and carbon monoxide reversibly. Peroxidase containing iron(II) absorbs CO but is oxidized by O_2, indicating that there is a hydrogen on one of the atoms bound to the iron. If the iron-nitrogen distance is increased, as by heat, the iron-oxygen bond is also weakened(9). The spin multiplicity of the oxygen is changed by the interaction with haemoglobin(5). All ferro-porphyrin complexes of unsaturated bases can carry oxygen, but no complex of a saturated base has this ability.

The oxygen is labile, even though the complex is covalent. Therefore, the iron is in an energy state only slightly more stable than its high-spin states.

It has been noted that the fourth oxygen to be absorbed shows the greatest affinity(1). Another interesting phenomenon is the Bohr effect. Haemoglobin is a stronger acid than oxy haemoglobin between pH 6.1 and 4.5, whereas the reverse is true between pH 6.1 and 9.0 (1). This is accounted for (16) by the presence of two independent oxygen-linked acid groups per haem, one of which is strengthened and the other weakened when haem combines with oxygen. The Bohr effect is lessened at high ionic strength. It is thought (17) that haemoglobin dissociates into two molecules at high ionic strength in neutral solution.

Wang(18) has developed a film having the properties similar to haemoglobin, in an attempt to determine the structural requirements for this behavior.

ROLE OF IRON IN REACTIONS

Catalase is known to be involved in oxidation of substrate by peroxides. This behavior has been observed with metmyoglobin, methaemoglobin, and peroxidase(6). All these are iron(III) complexes, and George(19) presents the intermediates as containing iron(IV), with oxygen bound in the sixth coordination position. The other alternative would be for the porphyrin to support the

charge and the iron(III) to be low spin. Both hypotheses are supported (6) by the magnetic moment corresponding to two unpaired electrons, oxidation equivalent of one, charge-transfer bands at 600 mμ and 450 mμ, and Soret band displaced to the red. However, the fact that the Soret band retains its usual intensity indicates that the porphyrin ring has not been attacked. Kinetic studies further support this(20). Electron spin resonance work(21) suggested that the electron was removed from the porphyrin but later work (22) showed the radical concentration to be too low to explain the amount of oxidation. George has argued that the radicals were merely a by-product(23).

Dwyer has contended(24) that too much emphasis is being placed on the iron, which should be thought of as only stabilizing the oxidation product of the organic group. Many reactions involving these complexes appear to be outer-sphere, since no more groups can get close to the iron. Electron exchanges would then appear to occur at the outer fringes of the organic group rather than at the iron. Perhaps the possibility of hydrogen-atom transfer should also be considered as a mechanism.

An example of outer sphere reduction with a haemoprotein as catalyst was suggested by Williams(9).

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Table I STRUCTURES OF THE HAEMOPROTEINS

Haemoprotein	Porphyrin	Substituent Placement	Function	Donor Molecules
Haemoglobin	Proto (2) 4 haems per unit (15)	CH_3, 1,3,5,8 (2) $CH=CH_2$ 2,4 CH_2CH_2COOH 6,7	O_2 transport(2)	2 imidazoles, 1 weak (5) or 1 imidazole, 1 H_2O
Myoglobin	Proto (2) 1 haem (15)		O_2 storate (2)	1 imidazole, 1 H_2O (5)
Chlorocruorin	Spirographis (2)	CHO 2 (2) $CH=CH_2$ 4 CH_2CH_2COOH 7,3	O_2 transport(?)(2)	
	or Rhodo (4)	$CHOHCH_2R$ 2 (7) $CH=CHR$ 4 CHO 8		
Catalase	Proto(FeIII)(2) 4 haems (15)		Catalytic decomp.(2) of H_2O_2	2 carboxylates (5)
Peroxidase	Proto(FeIII)(2) 1 haem		Oxidize substrate(2) with H_2O_2	amine-carboxylate(5) or carboxylate-H_2O
Cytochrome a	Rhodo (4)		Cellular Respiration(2)	2 imidazoles, 1 weak(5)
Cytochrome a_2	Dihydro (4)	$CH=CHR$ (4) $CHOHCH_2R$ 1 partly saturated pyrrole		
Cytochrome a_3	Rhodo (4)		Cellular Respiration(2)	1 imidazole, 1 H_2O
Cytochrome b	Proto (2)		Cellular Respiration(2)	1 amine, 1 imidazole(5)
Cytochrome c	Similar to (4) Meso or Hemato C: 1 haem (15) C_1:4 haems	CH_3 1,3,5,8 (7) $CHSHCH_3$ 2,4 CH_2CH_2COOH 6,7	Cellular Respiration(2)	2 imidazoles (5)
Cytochrome C_3	Haemato-type(4)			
Cytochrome d	Haemato-type(4)	No unsaturates (5)		1 amino, 1 H_2O (5)
Cytochrome f	Haemato-type(4)			

Table II DATA ON THE HAEMOPROTEINS

Haemoprotein	Spin of Fe(III)	E_o	α, ε	β, ε	Soret, ε	CTB, ε Fe(III)
Haemoglobin	high (4) 5.65 B M (6)	-0.15(4)	590,5 FeIII580(5)	550,13 (9) 540(6)	430(5) 405 170(5)	500,10.0(6) 631,4.4(6)
Myoglobin	high (4) 5.73 B M (6)	-0.02(4)	(9) FeIII580(6)	555,15 (9) 5[illegible]	435(5) 408,138(6)	500,10.2(6) 630, 3.9(b)
Chlorocruorin	high (4)	-0.20(4)	605 ?,12 (9)	565,12 (9)		
Catalase	5.29 B M (6)		585,9.5 (6)	537,13.2 (6)	407,138 (6)	490,17(6) 622,10.5(6)
Peroxidase	(OH^-)2.66 (25) (H_2O)5.48 (6)		580,2.5(6)	550,7.5 (6)	400(5) 403,91(6)	497,10.0(6) 641,2.8 (6)
Cytochrome a	mostly low(4)	-0.28(4)	605,hi (9)	560-70,lo (9)	444?(5)	
Cytochrome a_2	high/low(4)	-0.30(4)				
Cytochrome a_3	high/low(4)	-0.30(4)	605,hi (9)	560-70,lo (9)	448(5)	
Cytochrome b	low (4)	0.00±0.08(4)	558,29 (9)	528,16 (9)	425(5)	
Cytochrome c	mostly low(4) 2.14B M (25)	-0.15±0.25(4) -0.262 (2)	550,29 (9)	520,29 (9)	415(5)	
Cytochrome c_3	low (4)	+0.20 (4)				
Cytochrome d	high (4)	0.00 (4)			423(5)	
Cytochrome f	high/low (4)	-0.36(4)				

Note: ε is a millimolar extinction coefficient

ANTIFERROMAGNETISM IN SOME FIRST-ROW TRANSITION-METAL FLUORIDES

J. C. Schapiro November 6, 1962

INTRODUCTION

The chemistry of simple and complex transition-metal fluorides has recently been discussed in two review articles (1,2); the major portion of the material contained in these articles will not be further considered. For the most part, we shall be interested in the behaviour of the first-row transition-metal fluorides in the solid state. Guggenheim(3) has described the preparation of single crystals of some transition-metal fluorides, which has facilitated x-ray and NMR studies.

Fluoride ion is considered to be a weak-field ligand as is evidenced by its position in the spectrochemical series(4), and as such should give rise to high-spin (paramagnetic) complexes. It should be noted that Ferguson, Knox and Wood(5) have found in a study of the absorption spectra of solid K_2NaCrF_6 and CrF_3 (both contain CrF_6 octahedra but, next nearest neighbors differ) that the calculated Dq for these compounds differ by 900 cm^{-1}. Therefore, the environment surrounding the ligand has a pronounced effect on the splitting of the d-orbitals. The field in CrF_3, which contains Cr-F-Cr bridges, is weaker. It is generally found that fluoro complexes are paramagnetic, the $[NiF_6]^{2-}$ ion is the only known fluoro complex of a first row transition-metal ion which is diamagnetic(6). However, many of these oomplexes, the magnetic susceptibility curves of which show typical paramagnetic behaviour at room temperature and above, show a decrease in magnetic susceptibility (antiferromagnetic behaviour) as the temperature is decreased.

ANTIFERROMAGNETISM

The unusual properties of an antiferromagnetic compound, below its Néel point, are due to interionic interactions which are comparable to the thermal energies at the Néel point and which become greater than thermal energies with further decrease in temperature. In addition to the maximum point in the magnetic susceptibility curve, the transition from a disordered paramagnetic to an ordered antiferromagnetic structure is also indicated by λ-type peaks in the specific heat and thermal expansion (7). It is evident, in some materials, that magnetic interactions can not be direct dipole-dipole interactions and that coupling of the dipoles takes place through intermediate ions. Cooperative magnetism of this type is found in many transition-metal fluorides and oxides.

EXCHANGE MECHANISMS

The exchange mechanisms proposed by various investigations have been qualitatively reviewed by Blackman(7). Kanamori(8) has considered the superexchange interaction in terms of the symmetry properties of electron orbitals. Early development of

exchange mechanisms excluded the possibility of non-orthogonal orbitals. In the crystal, the orbital of the cation and those of the anions overlap considerably; therefore, they are not orthogonal, except when the orbitals have certain different symmetry properties. Yamashita and Kondo(9) have studied the superexchange interaction in MnO using the Heitler-London model and have included overlap (non-orthogonality) among the electron orbitals.

1. SUPEREXCHANGE-ANDERSON MODEL

The first superexchange mechanism was developed by Anderson(10) and was initially applied to the MnO system. Consider a system of two magnetic ions, such as the Mn^{2+} ion separated by an O^{2-} ion, which has the following colinear configuration

$$Mn^{2+}\ (\underline{d}_1)\text{-}O^{2-}(\underline{pp'})\ \text{-}Mn^{2+}(\underline{d}_2)$$

where $\underline{d}_1$ and $\underline{d}_2$ represent the total (five) unpaired electrons in the $3\underline{d}$ levels of the Mn^{2+} ions and $\underline{p}$ and $\underline{p}'$ represent the two electrons in the bonding $2\underline{p}$ orbital of the oxygen ion. There is a finite possibility that one electron will jump from the O^{2-} ion into the $3\underline{d}$ level of an Mn ion, becoming $\underline{d}'$ (or alternatively into an $\underline{s}$-state, which is coupled by some strong spin-dependent interaction with $\underline{d}$ electrons on the magnetic ion. According to the Pauli principle, the spin of the transferred electron will be antiparallel to the resultant spin of the electrons ($\underline{d}_2$) already present. A mixture of the original ground state with the following state

$$Mn^{2+}(\underline{d}_1)\ \text{-}\ O^{-}(\underline{p})\ \text{-}\ Mn^{+}(\underline{d}_2\underline{d}')$$

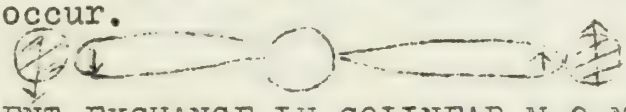
will be of lower energy than the original ground state. The electron ($\underline{p}$) remaining on the oxygen ion can couple with the magnetic electron on the magnetic ion to which the electron has not been transferred. Since the electrons originally on the oxygen ion had antiparallel spins there will appear to be an indirect negative exchange (antiferromagnetic) coupling between the spins of the two Mn ions.

It should be emphasized that the Anderson mechanism is a combination of two processes: (1) electron transfer, and (2) a

coupling process. Therefore, the Anderson model gives rise to antiferromagnetic interaction between cations with more than half-filled d shells and a ferromagnetic interaction between cations with less than half-filled d-shells. In the case of a less than half-filled d-shell, the spin of the transferred electron would be parallel (Hund's rule) to the resultant spin of the electrons on the magnetic ion. The conclusion for the less than half-filled d-shell is, however, not always supported experimentally, e.g., $CaMnO_3$ is antiferromagnetic.

2. SEMI-COVALENT EXCHANGE-GOODENOUGH MODEL

Goodenough and Loeb(11) and Goodenough (12) have proposed a model for superexchange which takes into account the mixing of 4s and 4p orbitals on the cation. Again, we shall use MnO as an example. In the crystal both lobes of an O^{2-} p orbital may overlap with an empty cation orbital. For coordinate covalence the O^{2-} orbital and empty cation orbital should be nearly degenerate. In ionic crystals, this is not the case for the ground state of the ion. However, if the cation has a net spin, exchange energy is gained if one of the two electrons in the oxygen p orbitals is excited to become part of the cation, thus forming a one electron "semi-covalent" bond. "Semi-covalence is defined as a bond due to the coupling of a single anion electron to the net spin of a cation (parallel spins). The other anion electron, therefore, has spin antiparallel to the spin of that cation. This other electron may participate in semi-covalence with a cation on the other side of the anion, and the spins of the two cations would be coupled antiparallel to each other. If the spins of the cations are parallel, semi-covalent bond formation can not occur.



SEMI-COVALENT EXCHANGE IN COLINEAR M-O-M SYSTEM

3. SLATER MODEL

The Slater model, as described by Yamashita and Kondo(9), takes into account the polarization of the electron cloud of the anion through the exchange energy with the cations. Again, consider the O^{2-} ion between two Mn^{2+} ions in a ^6S state, the spins of which are antiparallel. Since exchange interaction and overlap interaction are effective only between the electrons of the same spin orientation, the charge cloud of one (2p0) electron of the O^{2-} ion with the positive spin orientation may polarize in such a way as to approach the one Mn^{2+} ion with opposite spin and to go away from the other Mn^{2+} ion with the same spin. In this case the internal energy (promotion of the election from 2p to 3s level) of the O^{2-} ion increases, but the loss will be compensated by the gain of the interaction energy. As for the other (2p0) electron with the negative spin orientation, the situation is the same. The other four electrons (2p, 1, -1, α, β) may also polarize but to a lesser extent. Here α refers to an electron with +1/2 spin and β to an electron with -1/2 spin. The configuration corresponding to the Slater model is the following $[Mn^{2+}, O^{2-}(2p)^6]+[Mn^{2+}, O^{2-}(2p\alpha)^2(3S\alpha)-(2p\beta)^3] + [Mn^{2+}, O^{2-}, (2p\alpha)^3(3S\beta)(2p\beta)^2]$

A fourth mechanism, designated as the double-exchange(7) interaction and pertaining to ferromagnetic behaviour in mixed oxides will not be discussed.

Wollan and co-workers(13) have considered the exchange mechanism in relationship to the structure observed in perovskite lattices (MF_3 and $KMnF_3$ compounds) The $\underline{d}_{x^2-y^2}$ and $\underline{d}_{z^2}$ orbitals are the ones which overlap the $\underline{p}$ orbitals of the intervening anions in this type of structure, and therefore these are the orbitals which would be expected to be associated with the indirect magnetic exchange in compounds having a perovskite structure. The observed magnetic data(13,14) can be accounted for on the basis of the following types of indirect exchange:

(a) Whenever half-filled orbitals of two magnetic cations overlap, respectively, the two lobes of a given $\underline{p}$ orbital, the magnetic exchange will be antiferromagnetic.

(b) Whenever empty orbitals of two magnetic cations overlap, respectively, the two lobes of a given anion $\underline{p}$ orbital, the magnetic exchange is likewise antiferromagnetic.

(c) Whenever an empty orbital of one magnetic ion overlaps one lobe of an anion $\underline{p}$ orbital and the other lobe of the same anion $\underline{p}$ orbital overlaps a half-filled orbital of another magnetic ion, the magnetic exchange is ferromagnetic.

TECHNIQUES FOR INVESTIGATION

The two major physical methods which are employed in the experiments to be considered in the following sections are neutron diffraction and paramagnetic resonance (NMR and ESR). Angular variation in the paramagnetic resonance spectra reflects the local symmetry(15). The three types of symmetry to be considered are (1) symmetry of the crystal (2) symmetry of the paramagnetic susceptibility, and (3)local symmetry of the paramagnetic complex. Hyperfine structure may be observed if a ligand Y has a nuclear magnetic moment. If the electron orbits of the X ion overlap those of the Y ions, the order of magnitude of the hyperfine structure is given by the product of the hyperfine structure of the free atom X and the probability of finding the unpaired electron on Y. Therefore, this splitting is observed in the ESR spectra of the magnetic ions and in addition is also observed in the NMR spectra of diamagnetic ligands. Tinkham(16) first applied this technique to fluoride by observing the ESR spectrum of Mn^{2+} in a ZnF_2 crystal.

MAGNETIC BEHAVIOUR OF THE FLUORIDES

1. MF_2 COMPOUNDS

Neutron-diffration studies(17) of MnF_2, FeF_2, CoF_2, and NiF_2, at low temperatures showed the super lattice structure characteristic of antiferromagnetism. These compounds crystallize with a rutile lattice, and the magnetic cell was found to have the same dimensions as the chemical unit cell; the moments of the magnetic ions at the lattice corners being antiparallel to the

moments of the body-centered ions. The alignment of the magnetic moments for MnF_2, FeF_2, and CoF_2 was found to be along the tetragonal axes.

Shulman and Jaccarino(18,19) investigated the F^{19} resonance in an oriented single crystal of MnF_2 between 68°K. and 300°K. They attribute the large shift observed from the F^{19} resonance in a diamagnetic field to the promotion of an electron from the F^- ion to the Mn^{2+} ion. It is thus a measure of the super-exchange interaction. However, in MnF_2 the F^- ions have C_{2v} site symmetry, and the Mn^{2+} ion has D_{2h} site symmetry. This low symmetry introduces uncertainty into the direction of the orbitals containing unpaired spins and complicates the interpretation of the data in terms of F^- ion orbitals .

2. KMF_3 COMPOUNDS

Okazaki and Suemune(20,21) have examined the crystal structures of $KMnF_3$, $KFeF_3$, $KCoF_3$, $KNiF_3$, and $KCuF_3$ above and below their Néel temperatures(20). All except $KCuF_3$ are of the cubic perovskite type at room temperature.

Compound	(T_N °K)	Crystal Structure Above T_N	Crystal Structure Below T_N
$KMnF_3$	88	Cubic	Monoclinic
$KFeF_3$	113	Cubic	Rhombohedral
$KCoF_3$	114	Cubic	Tetragonal(a>c)
$KNiF_3$	275	Cubic	Cubic
$KCuF_3$	243	Tetragonal(a>c)	Tetragonal

Scatturin, Corliss, Elliott and Hastings(14) have studied the antiferromagnetic structures of $KCrF_3$, $KMnF_3$, $KFeF_3$, $KNiF_3$, and $KCuF_3$ *via* neutron diffraction. The Mn, Fe, Co, and Ni double fluorides exhibit an ordering in which the divalent 3*d* ion is coupled antiferromagnetically to its six nearest neighbors. In the Cr double fluoride, the magnetic structure consists of ferromagnetic (001) sheets, coupled antiferromagnetically along the [001] direction. The authors were not able to observe any magnetic scattering in the neutron-diffraction pattern of $KCuF_3$. The compound $KMnF_3$ is an example of a substance which has been studied by both EPR and NMR techniques. Shulman, Knox, and Wyluda(23) and Shulman and Knox(24) have studied the NMR of F^{19} and measured the hyperfine interactions between the F nucleus and the magnetic electrons. The isotropic hyperfine interaction constant *A*s was found to be $(16.26 \pm 0.4) \times 10^{-4}$ cm.$^{-1}$, which corresponds to (0.52 ± 0.02)% 2*S* character for the unpaired electron, whereas the anisotropic constant ($A_\sigma - A_\pi$) is equal to $(0.17 \pm 0.1) \times 10^{-4}$ cm.$^{-1}$, which corresponds to (0.18 ± 0.1)% 2*p* character. An antiferromagnetic transition evidenced by changes in the resonance pattern was observed at 88.5°K. Ogawa(25) measured the EPR of $^{55}Mn^{2+}$ ion as a dilute substitutional

impurity in single crystals of $KMgF_3$(essentially have $RMnF_3$ environment), $KCdF_3$, K_2MgF_4, and $NaMgF_3$. The $\underline{A}$s in $KMnF_3$ was estimated to be somewhat smaller than 16.7×10^{-4} cm.$^{-1}$ from the observed results.

Shulman and Knox(26) have also measured the NMR of F^{19} in single crystals of $KNiF_3$. Since this crystal has high symmetry (perovskite structure), the resonance shifts observed were interpreted directly in terms of the fraction of unpaired spins in the F^- ion $2\underline{s}$, $2\underline{p}_\sigma$, and $2\underline{p}_\pi$ orbitals. Large amounts of both $\underline{P}_\sigma$ an $\underline{P}_\pi$ interactions with the $\underline{d}$ electrons was indicated.

3. K_2MF_4 COMPOUNDS

The most interesting of these is the Cu^{2+} compound, which has been shown by Knox(27) to have two short Cu-F bonds and four long Cu-F bonds. It is isostructural with K_2NiF_4. However, whereas the Ni^{2+} compound is strongly antiferromagnetic the Cu^{2+} compound is not(28). This has been shown to be a result of the peculiar structure and the electronic configuration in this compound, which rules out any superexchange interaction.

CONCLUSION

Antiferromagnetic behaviour in the first-row transition-metal fluorides considered is the result of some type of superexchange mechanism . The mechanism of superexchange in transition-metal fluorides is strongly dependent upon the electronic configuration and site symmetry of the metal ions and the crystal symmetry of the compounds.

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This leads to the energy levels

$$E_+ = H_o + \frac{\gamma}{2} + [(\frac{\gamma}{2})^2 + 2\beta^2]^{1/2}$$

$$E_o = H_o - \gamma$$

$$E_- = H_o + \frac{\gamma}{2} - [(\frac{\gamma}{2})^2 + 2\beta^2]^{1/2}$$

Only one bonding orbital is available for all values of γ/β. When $\gamma/\beta = 0$, the bonding orbital is

$$\psi_+ = \frac{1}{2} (\phi_A + \sqrt{2}\ \phi_B + \phi_C)$$

When $\gamma/\beta = 1$,

$$\psi_+ = (\frac{1}{\sqrt{3}}) (\phi_A + \phi_B + \phi_C)$$

When $\gamma/\beta = 0$, an open type bond results; when $\gamma/\beta = 1$, a central bond forms.

Hamilton(10) has performed a four-center, four-electron calculation for diborane, and Yamazaki(11) has treated the problem as a twelve-electron system. Comparison of these results with that of the simple localized molecular orbital indicates that the three-center bond description is very accurate for diborane (12).

SEMI-TOPOLOGICAL TREATMENT

In an attempt to develop a systematic method of describing the electronic structure of the boron hydrides, Eberhardt, Crawford, and Lipscomb(2) presented a set of valence postulates and equations of balance. By applying semi-topological arguments together with the equations of balance, Dickerson and Lipscomb(13) have been able to limit the possible structures for the hydrides and make predictions as to existence and structure of the hydrides and hydride ions. (Platt (14) attempted a symbolic structure treatment, but his results are incompatible with the results of reference (2) and with the correct structure of B_9H_{15} (7)).

The equations of balance (15) are simple to derive. (See also 16, 3, 2). $[B_rB_pH_{P+q}]^c$ (general boron hydride formula) where r = number of boron atoms with no terminal hydrogen atom attached.

Let s = number of B-H-B hydrogen bridge bonds,
t = number of three-center B-B-B bonds,
y = number of two-center B-B bonds,
x = number of single B-H bonds in excess of one per boron.

Hydrogen atom balance: $s + x = q + c$
Orbital balance: $s + t = p + r + c$

Electron balance: $t + y = p + \frac{3r}{2} - c - \frac{s}{2}$

Boron hydride structures are tabulated in terms of s, t, y, and x. The following principles are the basis of the topological approach:

1. Assume that each boron atom must be chemically bonded to each adjacent boron atom by at least one two-center or three-center bond.

2. Define the connectivity of a boron atom as the number of other boron atoms to which it is adjacent in such a position as to allow bonding.

Define excess connectivity (EC) as connectivity minus 3.

3. Define the excess connectability of a bond arrangement at a boron site as the number of other boron atoms to which it connects the given one, minus the number of orbitals which it requires from the given boron atom.

Note that a B-B single bond or a B-H-B three-center bond produces no change in the EC of a framework.

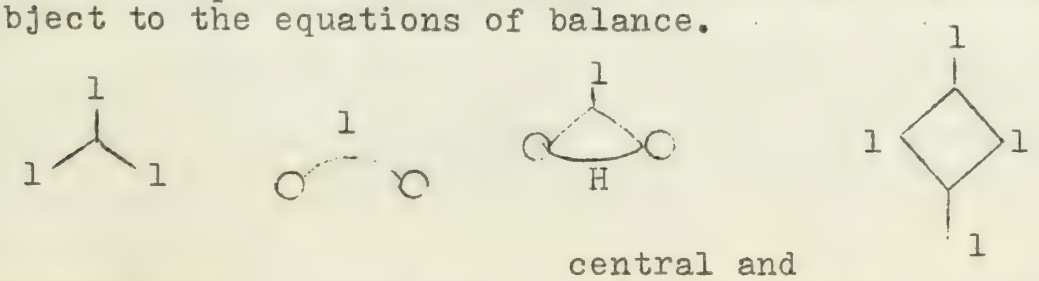
The procedure to be followed in looking for feasible boron hydride structures is:

1. Assume a boron framework and make a topological sketch of it, indicating the EC at each boron site.

2. Add extra B-H bonds to every boron atom of EC = -1, and possibly to certain boron atoms of EC = 0 or 1, but not to a boron atom of EC = 2.

3. Add three-center B-B-B bonds or arrangements of them in such a way that the EC at every boron site is reduced to zero.

4. Complete the molecule with B-B and B-H-B bonds, subject to the equations of balance.



Central bond | open bond | central and hydrogen bridge | adjacent central bond

Fig. 1. Excess connectabilities of various bonds.

To eliminate from consideration certain structural features not present among the known boron hydrides, these principles are applied in order of decreasing reliability:

(a) A new hydride would probably have at least a plane of symmetry or some other twofold symmetry element.

(b) No two adjacent boron atoms can be connected by both a central and an open three-center bond.

(c) Boron atoms of EC = 2 do not contribute to a B-H-B bridge or to an extra B-H, thus restricting B-H-B bridges to the edge of the framework, and BH_2 groups to the outer boron atoms.

(d) Each boron atom of EC = -1 will probably be bonded by one hydrogen atom to at least one of its two adjacent boron atoms.

(e) An edge boron atom of EC = 1 will probably not be connected to two other boron atoms by hydrogen bridges. This is the waakest assumption.

The justification of these five principles is ultimately the fact that they are generalizations from the presently known hydrides.

The importance of this topological extension of the valence theory is that it so dramatically reduces the number of likely structures in a given case. For example, B_4 yields the true B_4H_{10} structure uniquely. The composition B_7 yields no satisfactory structures based on an icosahedral fragment, and B_{10} yields only the established $B_{10}H_{14}$. (See (13),(16) for other results and predictions.)

This topological method can be extended to various other situations. It is invariant (15) with respect to replacement of H^- by an electron pair donor ligand L; replacement of H by D, a halogen, an alkyl group, or an aryl group; replacement of a bridge hydrogen by XR_2 to be bonded then by two X-B bonds, where X is N or P and R is H, an alkyl group, or an aryl group; replacement of a three-center bonded H^- by a three-center bonded CH_3^-, [illegible] substitution of hetero-atoms in the boron framework, e.g., C for B^-, Be for B^+, N for B^{-2}, Al for B. The topological treatment has also been used to study reactions and predict products (17). The boron hydride ions, the boron halides, and $B_xH_yO_z$ compounds have been treated in the same manner(16).

MOLECULAR-ORBITAL DESCRIPTIONS

Although the three-center bond concept is useful, the electrons in the more complex and symmetrical boron hydrides must be much more delocalized. Indeed, the localized bond theory does not and cannot predict accurate charge distributions. The molecular orbital approach is necessary for this.

In some of the simpler boron hydrides, the molecular orbitals can be formed readily by assuming the hybridization of the borons in the framework and combining these hybridized orbitals to fit the symmetry of the molecule(2,9,18). In compounds with low symmetry, it is not so obvious which combination will yield proper symmetry orbitals; so group theoretical treatment must be worked out in detail.

The basic assumptions employed in the molecular-orbital method are those used in the simple three-center bond treatment, but now there are many atoms involved. Also, $S_{jk} = S_{ik}$ is not a valid assumption for the boron polyhedra. All the overlap integrals must be evaluated, because the assumption of only nearest-neighbor interactions is not a reasonable assumption and leads to inconsistencies (19).

Longuet-Higgins (20) and Lipscomb(13) both predicted by molecular-orbital theory that a B_{12} hydride should exist as the $B_{12}H_{12}^{-2}$ ion. Just recently, the existence and structure of this ion has been determined(21).

An LCAO treatment of the boron framework orbitals in $B_{10}H_{14}$ yields a charge distribution which agrees with that expected from chemical behavior (22). An investigation of boron orbitals in the B_5H_5 molecule of D_{3h} symmetry indicates expected stability for $B_5H_5^{-2}$, but not for the neutral molecule (22).

The ion $B_{10}H_{10}^{-2}$ has been prepared. With D_{4d} symmetry postulated, its closed shell structure was predicted by molecular orbital theory (23).

The existence of $B_4H_7^-$ and $B_6H_{11}^+$, both related to B_5H_9, has been predicted because molecular-orbital treatment suggests these ions should be stable (24).

CONCLUSION

Many new hydride ions which have been predicted to be stable by both molecular-orbital and topological methods have been isolated. Their structures confirm the predictions and support the validity of these treatments (25, 26, 27). A crystal-field model, which has been developed for finding the molecular orbitals of identical atoms, is applicable to boron polyhedra (28). The molecular-orbital and semi-topological approaches are complimentary methods for the study of the bonding and structure of the boron hydrides. These principles can be extended to other electron-deficient systems and to metallic bonding (29).

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NUCLEAR QUADRUPOLE RESONANCE IN INORGANIC CHEMISTRY

Ronald H. Carlson November 20, 1962

INTRODUCTION

Nuclear quadrupole interactions in gaseous molecules were first discovered in an examination of the radiofrequency spectra of HD and D_2 using molecular beam spectroscopic methods (1). The first evidence for quadrupole interactions in the microwave spectra of gaseous molecules was obtained by Coles and Good (2) in their study of NH_3. Dehmelt and Krüger (3) in their investigation of trans-dichloroethylene were the first to observe direct radiofrequency "pure" quadrupole spectra of solids.

Since its early beginning in the past decade, nuclear quadrupole resonance (NQR) spectroscopy has proven itself an extremely useful tool for gaining additional insight into the chemical bonding of many inorganic compounds. Inasmuch as most of the current NQR literature deals with investigations of solid compounds, this seminar will be concerned primarily with data obtained from pure quadrupole resonance spectroscopy. However, some mention will be made of earlier data obtained from the microwave spectra of gaseous molecules. Several excellent reviews dealing with nuclear quadrupole resonance in both the solid and gaseous state are available (4,5,6,7,8,9,10).

THEORY

Nuclei, the spins of which are greater than 1/2, have a non-spherical charge distribution with respect to the spin axis. The magnitude of this departure of nuclear charge from spherical symmetry is measured by the nuclear quadrupole moment $\underline{Q}$. The usual definition of an electric quadrupole moment implies units of charge x distance squared. However, in defining the nuclear quadrupole moment it has been the convention to factor out the protonic charge and to express $\underline{Q}$ simply in terms cm^2 (6). Some of the more common nuclei possessing quadrupole moments are (12): H^2(D), Li^6, Li^7, B^{10}, B^{11}, N^{14}, O^{17}, Al^{27}, S^{33}, Cl^{35}, Cl^{37}, Br^{79}, Br^{81} and I^{127}.

When placed in an inhomogeneous molecular electric field, a quadrupolar nucleus is capable of undergoing a reorientation under the influence of an oscillating magnetic field of suitable radiofrequency. This reorientation phenomenon is called "nuclear quadrupole resonance". Each possible orientation of a nucleus with respect to the inhomogeneous molecular electric field is quantized, i.e. has a discreet characteristic potential energy. The energy of reorientation or interaction is directly proportional to the "nuclear quadrupole coupling constant" $\underline{eQq}$, where $\underline{e}$ is the protonic charge, $\underline{Q}$ the quadrupole moment, and $\underline{q}$ the average value of the electric field gradient. The quadrupole coupling constant has dimensions of energy, but by convention is divided by Planck's constant $\underline{h}$ to give it dimensions of frequency (usually megacycles per sec.).

Nuclear quadrupole resonances can be measured both in the solid state and in the gaseous state. In the former, they are measured directly in the long wave-length radiofrequency region, whereas in the latter they are measured indirectly as perturbations of rotational lines in the microwave region. From a theoretical standpoint at least, it is much easier to observe quadrupole resonances directly from radiofrequency spectra than indirectly from microwave spectra.

The field gradient q comprises a symmetric tensor having 9 components q_{ij} in the Cartesian coordinate system, where $q_{ij} = \frac{\partial^2 V}{\partial i \partial j}$ with ij representing the X, Y or Z Cartesian axis (4). V is the time-averaged electrostatic potential observed at the nucleus as arising from all charges residing outside of the nucleus. From symmetry considerations and from Laplace's equation: $q_{XX}+q_{YY}+q_{ZZ} = 0$, it is possible to reduce the number of q_{ij} components to 5. Further simplification of the system may be obtained by choosing a special set of axes in which all cross terms (q_{XZ}, q_{YZ}, etc.) become zero. This particular axis system is known as the "principal axis system", and in it the field gradient components are designated by small letter subscripts q_{xx}, q_{yy}, q_{zz} (6). The principal axis system is chosen by convention such that not only the cross terms become zero, but also $|q_{xx}| \leq |q_{yy}| \leq |q_{zz}|$ (I) One can go a step further in the simplification process and define a quantity η called the asymmetry parameter such that $\eta = \frac{q_{xx}-q_{yy}}{q_{zz}}$ (II). η can take on any value between 0 and 1. Where $\eta = 0$ there is axial symmetry around the z axis and $q_{xx}=q_{yy}= -1/2q_{zz}$. When $\eta \neq 0$, there is asymmetry around the z axis and the system becomes more complicated.

The quadrupole Hamiltonian may be expressed as (6)

$$H = \frac{e\,Q}{2I(2I-1)} \left(q_{xx} I_x^2 + q_{yy} I_y^2 + q_{zz} I_z^2\right) \quad \text{(III)}$$

where I_x, I_y, and I_z are the projections of the nuclear spin angular momentum upon the 3 principal axes. By constructing the Hamiltonian matrix elements and diagonalizing the resulting matrix, the eigenvalues of the Hamiltonian (the energy levels of the quadrupolar system) for axially symmetric fields ($\eta = 0$) can be obtained (13):

$$E_m = A\,[3m^2 - I(I+1)] \quad \text{(IV)}$$

Where I is the nuclear spin quantum number and m is the magnetic quantum number representing the projection of I upon the z axis. The term m can take on values ranging from I, $I-1$..., $-I$. The quantity A in the above expression is equal to $\frac{e\,Q\,q}{4I(2I-1)}$.

Since the two states $\pm m$ have the same energy, the above energy levels will be doubly degenerate.

The frequencies for quadrupolar transitions are given by the familiar relation $\Delta E = h\nu$ and the selection rule $\Delta m = i$. For spins of 1 and 3/2 there is only 1 transition frequency, for spins of 2 and 5/2 there are 2 transition frequencies, for spins of 3 and 7/2 there are 3 transition frequencies, etc. For nuclei such as Br^{79}, Br^{81}, Cl^{35}, Cl^{37} with $I = 3/2$, it can readily be shown that

$$E \pm_{1/2} = -1/4\ eQq \text{ and } E \pm_{3/2} = 1/4\ eQq$$

and that $\nu = \Delta E/h = 1/2\ eQq/h$ (V).

For N^{14} with $I = 1$, $\nu = 3/4 eQq/h$ (VI). However, I^{127} with $I = 5/2$ has two resonance frequencies with

$$\nu_1 = 3/20\ eQq/h \qquad \text{(VII)}$$
$$\nu_2 = 6/20\ eQq/h$$

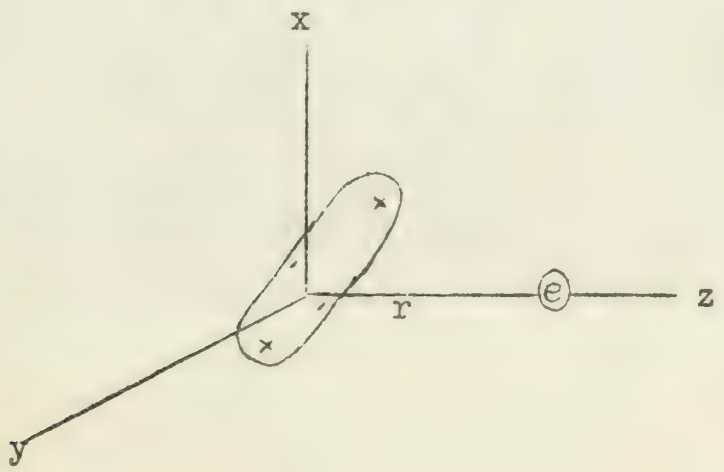
Measurement of the transition frequencies thus allows one to calculate the coupling constants directly in an axially symmetric field.

For nonaxially symmetric fields, the additional parameter η appears in the energy level expressions. For $I = 3/2$ ($\eta \neq 0$), measurement of the transition frequency alone is not sufficient to establish either eQq or η. However, by applying a magnetic field and observing the Zeeman splittings, these quantities may be readily determined. For $I = 1, 2, 5/2$ or greater, eQq and η may be determined directly from transition frequencies without having to resort to application of a magnetic field (6).

CORRELATION OF eQq WITH MOLECULAR STRUCTURE

As previously mentioned, the electric field gradient q in the principal axis system is composed of the three components $q_{xx} = q_{yy} = -1/2 q_{zz} = -1/2\ \partial^2 V/\partial z^2$. Now since $V = -e/r$, $\frac{\partial^2 V}{\partial z^2} = -2e/r^3$ for $\eta = 0$.

and $q_{zz} = e/r^3$. Thus q is directly proportional to $1/r^3$ for a charge at a distance r from the quadrupolar nucleus. This can be illustrated by Figure I.



By convention, the principal axis coordinate system is so chosen that the z axis coincides with the line of centers between the two charges along $\underline{r}$. When discussing molecules, one is interested in the case where the valence electron (-e) participates in a chemical bond with another atom. The z axis then often lies in the direction of the valence bond joining the two atoms, and hence $\underline{q}_{zz}$ is the component most sensitive to field gradient fluctuations brought about by variations in chemical bonding. The quantity q_{zz} has been shown to be inversely proportional to $\frac{1}{\underline{r}^3}$; thus it is to be expected that only those electrons which penetrate sufficiently close to the nucleus will have an effect on $\underline{q}_{zz}$. Townes and Dailey (14) have shown that the magnitude of $\underline{q}_{zz}$ at the nucleus is almost entirely dependent upon the electronic distribution in the valence $\underline{p}$ electronic shell. They state that any $\underline{s}$ orbital or any closed valence electronic shell is spherically symmetrical and hence gives no contribution to $\underline{q}_{zz}$ and that valence $\underline{d}$ and $\underline{f}$ orbitals do <u>not</u> penetrate sufficiently close to the nucleus to have an effect on $\underline{q}_{zz}$.

The contribution to the electric field gradient at the nucleus may arise from the following sources (9):

1) Valence electrons of the nucleus in quastion
2) Distortion of the closed shells of electrons around the nucleus
3) Charge distributions associated with adjacent atoms or ions.

Generally, to evaluate $\underline{q}$ at a particular nucleus in a molecule it is necessary only to consider contributions of type 1. However, when dealing with highly ionic molecules, contributions 2 and 3 become important and should be taken into account.

The first formal attempt to interpret observed nuclear quadrupole coupling constants and to correlate them with molecular electronic structure was made by Townes and Dailey in their discussion of some simple Cl compounds (14). They argued that since a neutral Cl atom has 5 valence $\underline{p}$ electrons and thus lacks <u>one</u> electron of acquiring a symmetrical closed-shell configuration, it would be expected to have a rather large quadrupole coupling constant. Townes and Dailey further state that for a Cl atom involved in a <u>covalent</u> bond, it would be a good approximation to say that it still has a <u>defect</u> of <u>one</u> valence $\underline{p}$ electron and hence should have a quadrupole coupling constant nearly as large as that for an isolated Cl atom. On the other hand, a Cl atom involved in a chemical bond with a highly electropositive atom such as Na or K has acquired a good share in another $\underline{p}$ electron and hence has a very nearly <u>symmetrical</u> closed valence shell. Under these circumstances, Cl would be expected to have an <u>eQq</u> value of zero or very close to zero. This effect can best be

represented by the following table:

Table I

Molecule	Structure	eQq(Mc/sec)
atomic Cl		-110.4
ClCN	Cl-C≡N	-82.5
CH_3Cl	$H_3\overset{+}{C}-\overset{-}{Cl}$	-75.13
NaCl	Na^+Cl^-	<1

From the very low value of eQq for NaCl, it was concluded that its bond was almost completely ionic in character. The table also shows that the eQq values for covalently bonded Cl are approximately 25% lower than the corresponding value for atomic Cl. Townes and Dailey attribute this, not to fractional ionic character, but to existing s-p hybridization of the covalent bond of an amount approximating 18%.

In a later paper (15), Townes and Dailey revised their estimates of s-p hybridization in halogens to include Br and I as well as Cl. They put forth a simple rule for the estimation of the amount of s character in a hybrid halide bond: Cl, Br and I bonds are taken to have 15% s character whenever the halogen is bonded to an atom which is more electropositive than the halogen by 0.25 of a unit, otherwise no hybridization is allowed. The authors defend this rule on the basis of observed quadrupole coupling data for halogens and on the basis of promotional energy considerations. Furthermore, they limit the amount of existing d character in halide bonds to 5% or less and in most cases consider it negligible.

Townes and Dailey (14) formulated the equations

$$eQq_{(mol)} = [(1-s+d)(1-i)]eQq_{(at)} \qquad \text{(VIII)}$$

$$eQq_{(mol)} = [(1-s+d)(1-i)+2(1+\epsilon)]\ eQq_{(at)} \qquad \text{(IX)}$$

for the quadrupole coupling of a halogen forming a hybrid bond with negative and positive ionic character i respectively; s and d are the amount of s and d character in the bond and ϵ is a constant (9), usually approximated to be 0.25, added to account for the fact that positive ionization increases q by pulling all of the electrons closer to the nucleus. The quantity $eQq_{(at)}$ is the coupling constant of an isolated atom and has been accurately determined for Cl, Br, and I by atomic beam measurements (9). Using molecule quadrupole coupling constants obtained from microwave spectra and employing equations (VIII) and (IX) and their hybridization rule, Townes and Dailey made a plot of ionicity vs. electronegativity difference for a series of diatomic halides. The curve revealed that for electronegativity differences greater than 2, molecules are essentially 100% ionic.

Gordy (16,17,18) has published a series of papers in opposition to Townes and Dailey's hybridization rule for halogens. He argues, on the basis of dipole moment considerations and observed coupling constants, that pure p orbitals are involved in Br, Cl and I bonds to all atoms except the two first row elements of C and F. Gordy defines a quantity

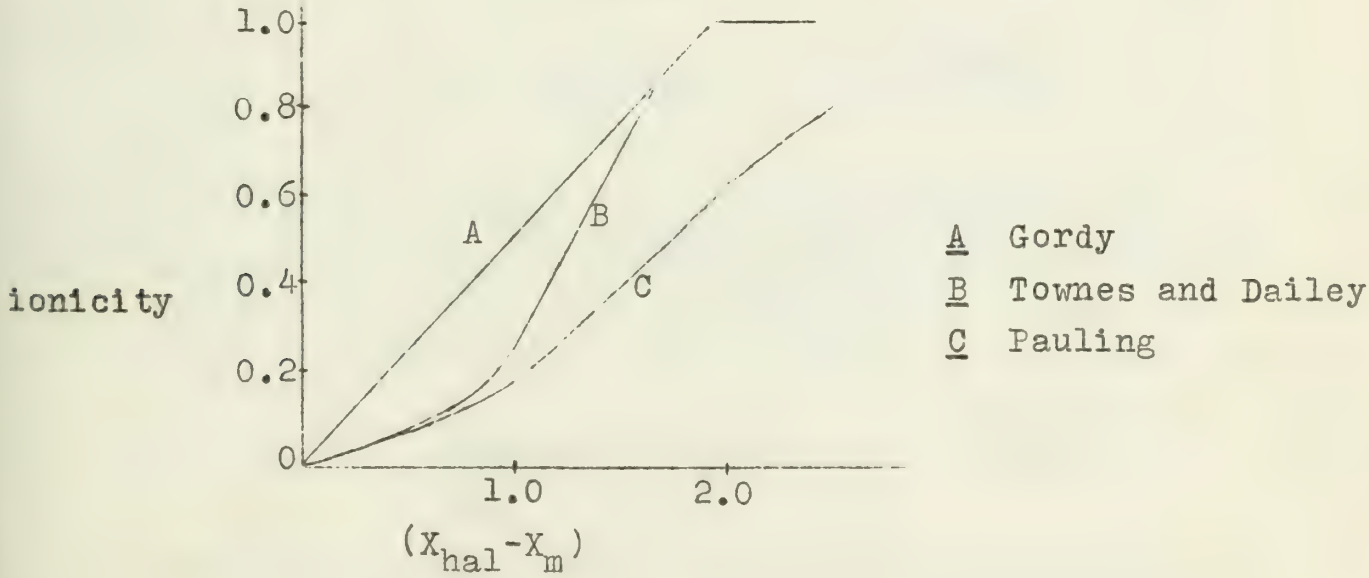
$$P_q = \left| \frac{eQq_{mol}}{eQq_{at}} \right| \qquad \text{(X)}$$

where $1-P_q$ is assumed to be equal to the ionicity of a molecule. He states that quadrupole measurements can be used to evaluate effective electronegativities of atoms bonded in various chemical groups since ionic character is a very sensitive function of electronegativity difference between atoms. For a series of diatomic halides and group (IV) polyatomic halides, Gordy made a plot of $1-P_q$ against electronegativity difference. From this curve, Gordy concluded that to a good approximation

$$1 - P_q = \frac{X_{hal}-X_m}{2} \quad \text{for } |X_{hal}-X_m| < 2 \qquad \text{(XI)}$$

where X_{hal} is the electronegativity of the halogen in question and X_m is the effective electronegativity of the atom bonded to the halogen. Gordy also concluded, as did Townes and Dailey, that for electronegativity differences greater than 2, bonding is essentially 100% ionic. Figure II gives a comparison between the Townes and Dailey, Gordy, and Pauling ionicity vs. electronegativity curves. Pauling derived his curve from dipole moment calculations made on hydrohalides (19).

Figure II



As can be seen, both the Townes-Dailey and Gordy curves differ quite markedly from Pauling's curve. This divergence can be explained by the fact that in his dipole moment calculations Pauling did not correct for the large overlap moment, which in the hydrohalides opposes the primary moment, and hence obtained low values of ionicity (18). The divergence between the Townes-Dailey and Gordy curves at lower electronegativity differences can be attributed to the different hybridization rules employed by the two groups of workers.

It is not possible on the basis of quadrupole measurements alone to draw conclusions as to whether Gordy's or Townes and Dailey's hybridization rule is the more nearly correct. Some experimental justification for the latter rule, however, has been obtained by Dailey (20) in his study of the halogen bond character of the alkyl halides. Dailey, using a modified form (4) of equation (VIII)

$$\underline{eQq}_{mol} = (1-\underline{s}+\underline{d}-\underline{I}-\underline{II})\ \underline{eQq}_{at} \qquad \text{(XII)}$$

and assuming negligible double bond character II and making an independent calculation of the ionicity $\underline{I}$, was able to determine the sum total of $\underline{s}$ and $\underline{d}$ hybridization for a series of 24 alkyl halides from observed coupling constants. The average values of $(-\underline{s}+\underline{d})$ calculated by Dailey were 13.6% for C-Cl bonds, 8.6% for C-Br bonds, and 1.8% for C-I bonds, in good support of the hybridization rule.

When using quadrupole coupling constants as the basis for correlating the molecular structure of a given family of compounds, it is best to define a quantity,

$$\underline{U}_p = \frac{\underline{eQq}_{(mol)}}{\underline{eQq}_{(at)}} \qquad \text{(XIII)}$$

called the "number of unbalanced $\underline{p}$ electrons directed along the bond axis" (9). With this quantity, one is able to compare coupling constants obtained from <u>different</u> quadrupolar nuclei. It should be observed that $\underline{U}_p$ has the same meaning as $\underline{P}_q$ defined earlier by Gordy (18). From equation (XII) one can see that

$$\underline{U}_p = \frac{\underline{eQq}_{mol}}{\underline{eQq}_{at}} = (1-\underline{s}+\underline{d}-\underline{I}-\underline{II}) \qquad \text{(XIV)}$$

and hence that there are $\underline{4}$ unknown parameters influencing $\underline{U}p$. The equation shows that $\underline{s}$ hybridization, ionicity, and double bond character all tend to <u>decrease</u> U_p, whereas $\underline{d}$ hybridization tends to <u>increase</u> $\underline{U}p$. It is quite apparent therefore that one single measurement of a molecular quadrupole coupling constant will not suffice to establish all $\underline{4}$ of the molecular parameters. Considerable insight can be gained, however, by studying related families of compounds where some of the parameters remain fairly constant or are zero, and by utilizing either Townes and Dailey's or Gordy's hybridization rule and ionicity curve.

Whitehead and Jaffé (46), in their investigation of the halogens and the interhalogens, have attempted to revaluate the relative contributions of orbital hybridization and ionic character to U_p. They state that neither the assumption of 0% s hybridization as proposed by Gordy, nor the assumption of a set 15% s hybridization as proposed by Townes and Dailey is reasonable or satisfactory when considering halogen bonding orbitals. The authors argue that orbital hybridization will occur only to the extent to match the energies of the bonding orbitals.

APPLICATION OF NQR TO GROUP IV HALIDES

Livingston (21, 22) has obtained the pure quadrupole resonance spectra of a series of chloro-substituted methanes. A regular decrease in eQq was observed in going from CCl_4 to CH_3Cl. Livingston explained this phenomenon by the fact that in going from CCl_4 to CH_3Cl, Cl is being replaced by a less electronegative element H, with the result that the effective electronegativity of C is decreased and hence the ionicity of the C-Cl bond is increased. This same trend in coupling constants was also observed by Robinson and coworkers (23) in their investigation of the pure quadrupole resonance spectra of bromo and iodo-substituted methanes. They too ascribed the decrease in eQq as originating from changes in the effective electronegativities of the bonding atoms as H is substituted for Br or I.

Mays and Dailey (24), using microwave spectroscopy, obtained the quadrupole coupling constants of a series of group IV halides of general formula MH_3X, where M=C, Si and Ge and X=Br and Cl. They interpreted the eQq values in terms of the % ionic character and % single bond and double bond character ot the M-X bond. Their calculations were based on the following assumptions:

1. Silane and germane derivatives have a double bond structure of the type $H_3M{=}X$ with metal d orbitals being employed in the bonding.

2. The carbon derivatives resonate only between the single bond covalent structure and the ionic structure i.e. $H_3C\text{-}X \longleftrightarrow H_3C^+X^-$.

3. In the double bond structure, $H_3M^-{=}X^+$, Cl and Br contribute a hybrid orbital with negligible d character and with 18% and 8% s character respectively to the σ component of the double bond. A pure p orbital is contributed to the π component of the double bond.

4. The % double bond character can be calculated using the equation: $y=(r_1-r_o)/r_1+2r_o-3r_2)$, where y is the fractional double bond character, r_1 and r_2 are actual M-X single and double distances respectively, and r_o is the observed internuclear distance of the molecule. Mays and Dailey's results are summarized in Table II. The authors assume an experimental error of 5% in their data.

Table II

Molecule	% double bond character	% single bond character	% ionic character
CH_3Cl	0	82	18
SiH_3Cl	29	34	37
GeH_3Cl	15	44	41
CH_3Br	0	82	18
SiH_3Br	25	34	41
GeH_3Br	15	46	39

In the light of these results, Mays and Dailey (24) were able to rationalize the fact that the dipole moment of GeH_3Cl is considerably greater than that of SiH_3Cl ($2.12 > 1.30$) despite the fact that the electronegativity difference between Ge and Si is very small. They state that increased π character in Si compounds tends to shorten the Si-X internuclear distance and hence decrease the dipole moment.

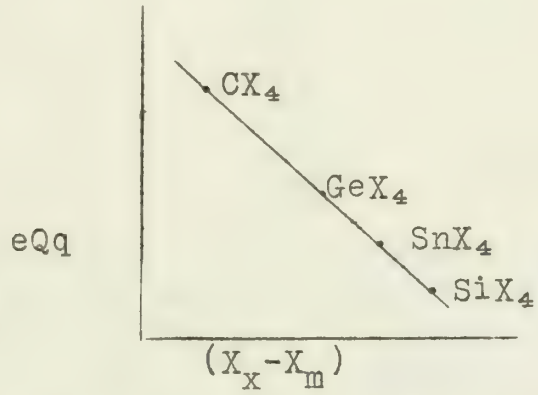
Schawlow (25) has interpreted the halogen quadrupole coupling constants obtained by him and others for a series of solid group IV tetrahalides. He used Townes and Dailey's hybridization rule and the same basic method of calculation of bond parameters as did Mays and Dailey (24). Schawlow's results showed increasing ionic character as the electronegativity difference between the group IV metal and the halogen increased. The agreement with Townes and Dailey's ionicity curve, however, was not very good(4), with only the data points obtained from GeI_4, SnI_4, CCl_4, and CBr_4 lying close to the curve. All other points were observed to lie somewhat below the curve, indicative of the fact that probably an excessive amount of double bonding was calculated for these compounds. Schawlow observed that the "number of unbalanced p electrons" U_p was less for the Si-halides than for any of the other M-halides. He interpreted this, not as an ionic effect with Si being the most electropositive group IV element, but rather, indicative of the fact that Si-X bonds have more π character than any of the other M-X bonds. Gordy (18), assuming negligible s and d character in halide bonding orbitals, re-valuated the molecular structure of the group IV tetrahalides from pure quadrupole spectra obtained by several groups of workers (21,22,23,25,26). His results, summarized in Table III, show the same trend in ionic character as noted above for Schawlow's data, but in general show a significantly smaller % double bond character.

Table III

Molecule	U_p observed	X_m	π character	Ionic Character	Single Bond Character
CCl_4	0.75	2.58	9	12	79
CBr_4	0.83	2.55	8	5	87
CI_4	0.93	2.50	4	1	95
$SiCl_4$	0.37	2.04	30	18	52
$SiBr_4$	0.46	1.98	26	15	59
SiI_4	0.58	1.96	20	12	68
$GeCl_4$	0.47	2.08	14	32	54
$GeBr_4$	0.54	2.03	12	27	61
GeI_4	0.65	2.00	9	21	70
$SnCl_4$	0.44	1.97	9	42	49
$SnBr_4$	0.50	1.91	8	37	55
SnI_4	0.61	1.87	6	31	63

Gordy's calculations of the effective electronegativity, X_m, of the central metal ion are particularly interesting, in that they show that Si is less electronegative than Ge, contrary to popular belief. It should be kept in mind that Gordy's electronegativity values are probably subject to some error since the error limits involved in factoring quadrupole coupling constants into components representative of the amount of π character, ionic character and orbital hybridization in a bond are quite large.

Allred and Rochow (27) interpreted some observed quadrupole coupling constants of group IV halides in terms of the electronegativity of the central metal group IV atom. They studied five series of group IV halides: MCl_4, MH_3Cl, MBr_4, MH_3Br, and MI_4 where M is C, Si, Ge, and Sn. For each series they obtained a plot of eQq vs. electronegativity difference of the following type:



From this evidence they concluded, that since Si-X compounds show the smallest halogen coupling constants, Si should be most electropositive of the 4 elements under investigation. Thus the following electronegativity order was postulated by Allred and Rochow as accounting for the observed linear relation between eQq and $[X_x-X_m]$: C > Ge > Sn > Si.

Drago (28) argues against Allred and Rochow's order of group IV electronegativities, stating that the quadrupole coupling constants of Si halides are lower than those observed for the corresponding Ge and Sn halides possibly due to the fact that additional π character and s hybridization exist in the Si-X bond. Drago states that the amount of s character in the M-X bond should decrease as one goes from C to Sn and hence that the quadrupole coupling constants of Si compounds should be lower than those for the corresponding Ge and Sn compounds as observed.

APPLICATION OF NQR TO OTHER HALIDE SYSTEMS

Nakamura and coworkers (29, 30, 31, 32) have obtained the pure quadrupole resonance spectra of a series of hexahalo platinates, palladates, tellurates, and stannates and have interpreted the data in terms of the covalency of the metal ligand bonds. The authors used equation VIII in their calculations and assumed 15% s character and negligible d character in the halide bonding orbitals. In addition, contributions to eQq from π character were assumed negligible. In each complex, the net charge ρ on the central metal atom was calculated from

the equation

$$\rho = 4-6(1-i) \qquad \text{(XV)}$$

where the quantity (1-i) represents the covalency of the molecule. The following table summarizes the results obtained by Nakamura and coworkers:

Table IV

Compound	% covalent character (1-i)	net charge (ρ)
K_2PtCl_6	56	0.64
K_2PtBr_6	62	0.28
K_2PtI_6	70	-0.20
K_2PdCl_6	57	0.58
K_2PdBr_6	63	0.22
$(NH_4)_2TeCl_6$	32	2.08
M_2TeBr_6	42	1.48
M_2TeI_6	52	0.88
K_2SnBr_6	40	1.60
$(NH_4)_2SnBr_6$	39	1.66

The coupling constants of the hexahalo-tellurates were found to lie very close to one another regardless of the cation ($M=NH_4^+$, K^+, Cs^+). Thus eQq was assumed to be governed by chemical effects rather than by crystal effects due to neighboring ions. The above equation was used in the calculation of ρ because each of the central metal ions in the hexahalides is formally tetrapositive but is surrounded by 6 halogen ions from which charges migrate in along coordinate bonds in accordance with the covalent character of the molecule. As can be noted from the table, the covalency of the stannates and tellurates is less than that of the platinates and palladates by as much as 20%. The authors explained this difference in behavior in terms of the electronic configurations of Te and Sn and the fact that Sn is somewhat less electronegative than Pt and Pd.

Hamlen and Koski (33) obtained the pure quadrupole resonance spectra of $TiCl_4$ and WCl_6 and interpreted their data using Townes and Dailey's procedure. Values of 87% and 77% were calculated for the ionicity of $TiCl_4$ and WCl_6 respectively. These values when plotted against electronegativity difference fell appreciably off Townes and Dailey's curve. This deviation was explained in terms of existing π character in the M-Cl bonds.

Reddoch (34) has investigated the compounds $TiCl_4$, $ThCl_4$, $NbCl_5$ and $TaCl_5$. He observed four resonance lines in the quadrupole spectra of $TiCl_4$ and hence postulated it to have a crystal structure similar to that of $SiCl_4$, $GeCl_4$ and $SnCl_4$, in the spectra of which four resonance lines were also observed (25). Reddock calculated a value of 87% ionicity for $ThCl_4$ using Townes and Dailey's procedure. He admitted this value might possibly be high, however, due to admixture of some π character in the bond. The spectra of $NbCl_5$ and $TaCl_2$ were discussed in terms of possible crystal structures for the compounds.

The covalent character of the paramagnetic halides $TiCl_3$, VCl_3, $CrCl_3$, and $CrBr_3$ was obtained by Barnes and Segel (35) from observed pure quadrupole coupling constants. They state that their values of covalency are in reasonable agreement with those based upon electronegativities of the bonding atoms.

SOLID STATE SHIFTS

The quadrupole coupling constant observed for a molecule in the solid state is usually 10% to 15% lower than the corresponding coupling constant observed for the molecule in the gaseous state (6). Some examples of this effect are noted in the following table.

Table V

Molecule	Nucleus	$\lvert eQq \rvert$ (Mc/sec) Gas	Solid	q_{solid}/q_{gas}
CH_3Cl	Cl^{35}	78.74	68.06	0.910
CH_2Cl_2	Cl^{35}	78.4	71.98	0.918
CH_3Br	Br^{81}	482	442	0.917
CD_3Br	Br^{81}	479.8	441	0.919
CH_3I	I^{127}	1934	1767	0.914
CD_3I	I^{127}	1929	1764	0.914

No absolute explanation of this solid state shift has as yet been proposed. O'Konski offers a general explanation for the shift observed in the alkyl halides in terms of an increase in ionic character in the crystal lattice resulting from an inductive charge transfer along the C-X bond produced by interaction between the molecular dipoles in the lattice. These solid state shifts are a function of the interaction of a molecule with its surrounding neighbors and hence are of considerable value when a knowledge of intermolecular forces, crystal structure, phase transitions and molecular motions in the solid state is desired.

N^{14} RESONANCES

The first N^{14} resonances obtained from pure quadrupole resonance spectroscopy were reported for BrCN and ICN by Watkins and Pound (36). Casabella and Bray (37) completed the investigation of the series when they reported the N^{14} resonance in ClCN. Townes and Dailey (38) postulated an intermolecular structure for solid ICN, in addition to the two resonance structures already known, to account for the fact that the coupling constant of I^{127} increases in going from the gaseous to the solid state. Casabella and Bray (37) extended the Townes and Dailey treatment to include ClCN and BrCN and using both N^{14} and halogen coupling constants were able to calculate the % importance of each resonance structure for the cyanohalogens in both the solid and gaseous state.

Negita and coworkers (39) have observed an N^{14} resonance in solid HCN. At liquid N_2 temperatures, two resonance lines appeared in the spectra, indicative of an asymmetry in the crystal. From their experiments the authors were able to determine the asymmetry parameter η quite easily without having to resort to the application of a magnetic field.

The pure quadrupole resonance spectra of NH_3 and ND_3 were obtained by O'Konski and Flautt (40). They state that the large decrease in the N^{14} coupling constant observed upon condensing gaseous NH_3 and ND_3, reflects increased ionic character in the solid state. They explained this enhanced ionicity in terms of resonance structures of the type

$$\geq N \cdots H^{+-} N \leq$$

involving H-bond formation, as being more important in the solid state.

MISCELLANEOUS RESONANCES

The quadrupole resonance spectrum of Al^{27} in the spinel $MgAl_2O_4$ showed that Al^{+3} ion occupies octahedral sites with rhombic point symmetry D_{3d} (41). Jones and Uehling (42) have obtained the pure quadrupole resonance spectrum of As^{75} in $Na_2HAsO_4.7H_2O$. A coupling constant of approximately 44 Mc/sec was reported. They were unable to obtain the spectrum of Na_3AsO_4 and attributed this to the tetrahedral symmetry of the isolated AsO_4 groups. Reddock has obtained a coupling constant of approximately 78 Mc/sec for Nb^{93} in $NbCl_5$. Due to the large asymmetry of the crystal (η =0.32), six resonance lines were observed instead of the usual four expected for a spin of 9/2.

The small quadrupole moment of the deuteron (43) and the predominantly spherical charge distribution near the nucleus combine to give deuteron quadrupole coupling constants of less than 1 Mc/sec. Hence any attempt to measure H^2 coupling constants must be done with spectrometers giving extremely high resolution. From measurements of hyperfine structure in the microwave spectrum of D_2O, Posener (44) obtained a coupling constant of 353 ± 4 Kc/sec for the deuteron in the direction of the OD bond. White (45) calculated the D coupling constants in DCN and DCCl from their pure quadrupole spectra and obtained values of 175 Kc/sec. and 290 Kc/sec.; he stated that the field gradient at the nucleus did not arise from any "unbalanced" p electrons, but was primarily due to charges residing on the adjacent C atoms and to overlap effects.

CONCLUSION

Nuclear quadrupole resonance techniques have been utilized to a great extent in the determination of the type of valence bonding in many halide compounds. It must be borne in mind that in the interpretation of the coupling constant one must consider all of the factors influencing it. The value obtained for the coupling constant of a given atom involved in a chemical bond is a function, not only of the ionicity of the bond, but of the degree of hybridization and π character existing in the bond as well.

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COMPLEXES OF o-PHENYLENEBIS(DIMETHYLARSINE)

L. V. Interrante November 27, 1962

INTRODUCTION

Among the species involving the arsenic atom as a donor, the complexes of o-phenylenebis(dimethylarsine)(PDA)(Fig. 1) have received by far the most attention.

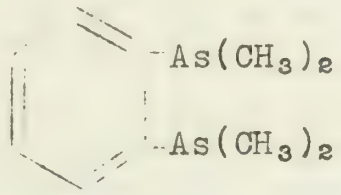


Fig. 1

This particular interest in PDA has been largely due to the increase in the stability of its complexes over those of the monodentate tertiary arsines, as a consequence of the chelate effect. The intensity of this interest is illustrated by the range of elements for which PDA complexes have been reported (Table I).

TABLE I - Elements Reported to Coordinate with PDA

IVa	Va	VIa	VIIa	VIII			Ib	IIb	IIIb	IVb	Vb
Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	-	-	P
Zr	-	Mo	Tc	Ru	Rh	Pd	Ag	Cd	-	Sn	As
Hf	-	W	Re	Os	-	Pt	Au	Hg	-	-	Sb
											Bi

PDA was first synthesized by Chatt and Mann in 1939(1). It was later employed by these workers in a study of the structure of bridged dipalladium derivatives (2). Approximately ten years later, Nyholm (3) began the series of investigations of PDA complexes which has been largely responsible for the extent of knowledge in this area to date.

THEORY

The study of the complexes of PDA is to a large extent the study of spin-paired, covalent complexes to which the valence-bond theory can be applied with considerable success. The low permanent dipole moment and high polarizibility of the tertiary arsine group are undoubtedly important factors promoting the formation of covalent complexes and hindering the formation of ionic complexes.

It has been suggested, however, that the major factor responsible for electron pairing and strong bonding in the PDA complexes is the capacity of the arsenic atoms to accept electrons from the metal in d - d bonding (4). The theoretical feasibility of double bonds in such complexes has been established from overlap integral calculations (4). Further support has been obtained from infrared spectral studies of substituted metal carbonyls (5,6). In particular, the infrared spectrum and dipole moment of the nickel carbonyl derivative, $[Ni(CO)_2D]$ [D = o-phenylenebis(dimethylarsine)], have been examined and interpreted to show that the bond order of the arsenic-nickel bonds in this compound is between 1.4 and 1.7 (6).

The coordination numbers of many of the transition-metal PDA complexes can be understood in terms of the tendency of the metal ion to make use of all nine orbitals (five (n-1)d, one ns and three np) for bonding pairs, for non-bonding pairs, or for single electrons (7). This "nine-orbital rule" may be thought of as an extension of the "inert-gas rule" for metal carbonyls. When the carbonyl groups are replaced by less strongly π-bonding groups, paramagnetism may arise with retention of the nine-orbital configuration for the complexed metal ion.

Table II (7) illustrates the dependence of the coordination number within each electronic configuration upon the number of unpaired electrons, which is, in turn, a function of the ligand field produced by metal ion and ligand.

TABLE II - Illustration of the Nine-Orbital Rule

Configuration	Unpaired Electrons	Coordination Number	Examples
d^0	0	9	-
d^1	1	8	$K_3Mo(CN)_8$, $[VD_2Cl_4]$
d^2	0 2	8 7	$K_3Re(CN)_8$, $[ReD_2Cl_4]ClO_4$ $K_4V(CN)_7$
d^3	1 3	7 6	$K_4Mo(CN)_7$ $K_3Cr(CN)_6$, $[CrD_2Cl_2]ClO_4$
d^4	0 2 4	7 6 5	$[MoD(CO)_3I_2]$ $[Cr(dipy)_3]^{2+}$, $[ReD_2Cl_2]^+$ $[MnDBr_2(H_2O)]Br$

It should be noted that this rule, although useful for many covalently bonded complexes, is not necessarily obeyed for more ionic complexes.

Provided that bonding orbitals are available, the main factors which seem to govern the tendency to assume a certain coordination number are (i) steric effects and (ii) the resulting charge on the metal ion (8). The second factor is considered to be of major importance in the majority of complexes (9).

The "electroneutrality principle" proposed by Pauling(10) suggests that metal ions tend to have a net charge of zero . Thus a metal ion will add ligands until its net charge, as determined by the degree of electron transfer in the metal-ligand bonds, is close to this value. Important among the factors which determine the degree of electron transfer is double bonding between metal and ligand (9). Consequently, ligands such as PDA which are capable of relieving the negative charge on the metal might be expected to lead to higher coordination numbers for that metal. This is supported in general for those cases in which d_π -d bonding is important, and is best exemplified by the preparation of five-coordinate PDA complexes of the d^7 and d^8 transition-metal ions (11, 12).

METAL DERIVATIVES OF PDA

The complexes of PDA with the transition metals are summarized in Tables III through VII. Discussion here will be confined only to those derivatives of particular interest.

A. Groups IVa and Va (Ti, Zr, Hf, and V)

Among the complexes of these metals with PDA, most noteworthy are the eight coordinate derivatives of the general formula $[MX_4D_2]$ (M = Ti, Zr, Hf, V; X = Cl, Br) (13, 14, 15). The titanium derivative, $[TiCl_4D_2]$, has been shown to have a dodecahedral structure by single-crystal X-ray analysis (14). This is the first example of a complex in which a first transition-series element exhibits eight coordination.

B. Group VIa (Cr, Mo, W)

The ability of PDA to enter into d_π - d bonding is illustrated by its replacement of carbon monoxide from metal carbonyls with retention of the formal zero-valent oxidation state of the metal.

In the case of the Group VI carbonyls, $[M(CO)_6]$, the derivatives $[M(CO)_4D]$ and $[M(CO)_2D_2]$ (M = Cr, Mo, W) (16, 17) have been obtained by reaction with PDA. The action of halogens upon these derivatives leads to further replacement of carbon monoxide and the formation of the complexes $[MoD(CO)_3X_2]$ and $[MoD_2(CO)_2X]X$ (X = Br, I) (7). These compounds are diamagnetic and molecular-weight and molecular-conductivity measurements in nitrobenzene indicate that they are seven-covalent derivatives of bivalent molybdenum. Thus with the strongly π-bonding carbonyl groups in addition to PDA, complete spin-pairing can occur,

leading to expansion of the coordination number in accordance with the nine-orbital rule.

C. Group VIIa (Mn, Tc, Re)

The complexes of bivalent manganese with PDA constitute the only known examples of spin-free, outer-orbital complexes involving this ligand. The failure of previous attempts (4) to prepare PDA complexes of manganese and the instability of the derivatives finally obtained (18) illustrate the reluctance of PDA to coordinate under these conditions. Complexes obtained are of the general formula $[MnD_2X_2]$ (X = Cl, Br, I).

The complexes of bivalent rhenium and technetium with PDA correspond to the same general formula $[MD_2X_2]$. However, they differ appreciably from those of manganese(II) in that they are spin-paired and of considerably greater stability (19, 20).

This difference is also exhibited by the tervalent derivatives of these metals, which include the spin-free, apparently five-coordinate $[MnDCl_2(H_2O)]ClO_4$ (18) and the spin-paired, six-coordinate $[MD_2X_2]Y$ (M = Tc, Re; X = Cl, Br, I; Y = ClO_4, X) (19,20). In this case, the reluctance of PDA to bond in an outer-orbital situation apparently results in a limitation of the coordination number of the manganese (III) derivative.

Oxidation of the tervalent rhenium and technetium derivatives yields a new series of diamagnetic, eight-covalent complexes of the type $[MD_2X_4]Y$, (M = Re, Tc; X = Cl, Br; Y = ClO_4, X), presumably containing the pentavalent metals (21, 22).

The partial replacement of carbon monoxide from the compound $Mn_2(CO)_{10}$ by PDA yields the complex, $[Mn(CO)_3D]$. Partial oxidation may be effected with halogen, leading, in the case of I_2, to the spin-paired derivative of univalent manganese, $[MnD(CO)_3I]$ (23).

D. Group VIII

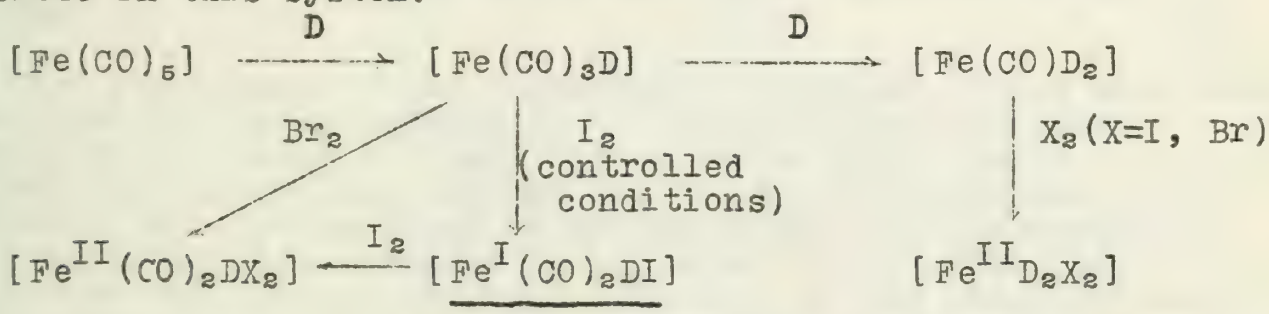
1. (Fe, Ru, Os)

In contrast to the isoelectronic manganese (II) ion, tervalent iron, ruthenium, and osmium, like rhenium(II) and technetium(II), yield six-covalent, spin-paired derivatives of the type $[MD_2X_2]Y$ (M = Fe, Ru, Os; X = halogen; Y = ClO_4, X) (3, 24, 25).

The ability of PDA to stabilize high as well as low oxidation states is illustrated by the oxidation of the tervalent iron and osmium complexes to the quadravalent compounds, $[MD_2X_2]Y_2$ (25, 26). This rather unusual oxidation state for iron is supported by magnetic measurements which indicate a d^4 configuration (26). Attempts to obtain the corresponding ruthenium(IV) derivative have as yet been unsuccessful (24).

The fact that complexes of the type $[MD_2X_2]$, as obtained with the iron group metals, should be capable of geometrical isomerism is illustrated by the reported isolation of cis-forms of the PDA and ditertiary phosphine complexes of ruthenium(II), $[RuL_2X_2]$ (X = halogen) (27). Unlike the trans forms previously obtained (24), the cis complexes are reduced by $LiALH_4$ to the complex hydrides $[RuL_2HX]$, which in the case of L = PDA are unstable and decompose upon standing (27).

Replacement of carbon monoxide from metal carbonyls, with subsequent oxidation by halogens, has been employed in the case of iron pentacarbonyl with the subsequent synthesis of a compound in which iron has a formal oxidation state of +1 (28). The following reaction scheme summarizes the conversions possible in this system:



The coordination number of five for the d^7 configuration of iron(I) is also exhibited by the isoelectronic species, manganese(0), cobalt(II), and nickel(III), in the complexes, $[Mn(CO)_3D]$, $[CoBr_2triars]$, and $[NiBr_3 2ET_3P]$. By adding one more electron, another series of isoelectronic ions exhibiting five-coordination is obtained. These include iron(0), i.e. $[Fe(CO)D_2]$; cobalt(I), i.e. $[Co(RNC)_5]X$; nickel(II), i.e. $[NiD_2X_2]ClO_4$; and gold(III), i.e. $[AuD_2X][ClO_4]_2$ (28). It should be noted that this is just the coordination number predicted by the nine-orbital rule for the d^7 and d^8 ions.

2. (Co, Rh)

Besides the reported preparation of the completely analogous rhodium(III) complexes (29), only the cobalt derivatives of PDA have been investigated in any detail.

Especially interesting are the tris-PDA complexes obtained for both cobalt(II) and cobalt(III), $[CoD_3][ClO_4]_2$ and $[CoD_3][ClO_4]_3$. These are among the few complexes prepared having more than two PDA molecules per metal ion (4).

Geometrical isomerism in the complexes of general formula $[CoD_2X_2]ClO_4$ has been established by means of absorption spectroscopy. By virtue of the reported proximity of PDA to ethylenediamine in the spectrochemical series, it has been possible to distinguish the cis and trans isomers of these complexes by direct comparison of their visible absorption spectra with those of the corresponding ethylenediamine complexes (30).

3. (Ni, Pd, Pt)

The tendency of the d^8 metals to assume a coordination number of five and the multivalency of nickel when coordinated to PDA may account for the particular attention afforded PDA complexes of this subgroup.

In addition to the derivatives of bivalent nickel of empirical formula NiD_2X_2 (X = Cl, Br, I, CNS, ClO_4) (31), complexes containing tervalent $[NiD_2X_2]\ ClO_4$ (31, 32) and quadravalent nickel $[NiD_2X_2][ClO_4]_2$ (33) have been isolated. The complexes obtained with platinum and palladium are entirely analogous to the nickel compounds except for the fact that no complexes of the tervalent state of either metal could be obtained (2, 8, 34).

The structures of the complexes of bivalent nickel mentioned above were initially assumed to be four-covalent and planar, largely on the basis of their diamagnetism (31). Later work, however, has shown that, except for the di-perchlorates, these complexes, as well as those of palladium(II) and platinum(II), are apparently five-covalent in solution (35, 34, 8). In support of this is the reported isolation of the monoperchlorate salts, $[MD_2X]\ ClO_4$ (M = Ni, Pd, Pt) and the preparation of a similar complex of methylbis(3-dimethylarsinopropyl)arsine, $[Ni(triars)Br_2]$ (36), which has been shown by single-crystal X-ray analysis to have a distorted square-pyramidal structure (37). The fact that this does not necessarily imply that the PDA complexes are similarly coordinated in the solid is indicated by X-ray work on the compound PdD_2I_2, which crystallizes in the form of a distorted octahedron (8). Furthermore, the possibility that some interaction along the sixth coordinate is provided by the solvent molecules in solutions of these complexes must not be ignored (34, 12).

Replacement of carbon monoxide in the nickel-group metal carbonyls has led to a series of new PDA complexes. Partial replacement yields the nickel complex $[Ni(CO)_2D]$, which may be converted to a previously unknown class of cis-planar nickel complexes, $[NiX_2D]$ (X = I, Br) (38) by treatment with halogen. Complete replacement has also been effected by heating $[Ni(CO)_2D]$ with PDA in vacuum, leading to the zerovalent nickel complex $[NiD_2]$ (28). This compound and its palladium analog have also been prepared by direct reduction of the corresponding dipositive cationic species using sodium borohydride (39).

E. Group Ib (Cu, Ag, Au)

Complexes of PDA with the Group Ib metals invariably involve either the univalent or tervalent metals. In no instance, including copper, has a complex of the bivalent metal been obtained. This statement may be extended to include the d^9 configuration in general for which no PDA complex has been reported.

The complexes of the univalent metals are isomorphous, four-covalent, presumably tetrahedral species of the type $[MD_2]Y$ (M = Cu, Ag, Au) (40, 41, 42, 43, 44). This coordination number, although commonly exhibited by copper(I), is rather unusual for gold(I), which as a rule prefers two-coordination. In this case the use of PDA is thought to favor formation of four-covalent structures since the chelate group prevents the use of linear sp bonds and so favors the addition of a second molecule of PDA (42).

In the case of gold these compounds may be oxidized to complexes containing the tervalent, d^8 ion. These include compounds in which gold appears to be four- five- and six-covalent (42). The bonding in these complexes is explained on the basis of valence-bond theory to involve the $6p_z$ and hybrid $6p_z 6d_z$ orbitals in addition to the $5d6s6p^2$ combination in the square, to account for five- and six-coordination, respectively (43, 42).

Due to the diffuse nature of the $6d_z$ orbital, it is expected that highly polar bonds would be formed. This is consistent with the conversion of the six-covalent derivatives to five-covalent complexes in water (43).

The electroneutrality principle has been employed to explain both the tendency of four-covalent gold(III) to expand its coordination number and the increased stability of the five-coordinate gold(III) complexes over the isoelectronic five-coordinate palladium(II) compounds (42).

F. Group IIb (Zn, Cd, Hg)

Reports of complexes involving the Group IIb metals and PDA have been confined to derivatives of the bivalent (d^{10}) metal ions. As expected these are characteristically four-coordinate and presumably tetrahedral, consisting of the non-electrolytes $[MDX_2]$ and the salts $[MD_2]\ (ClO_4)_2$ (M = Zn, Cd, Hg; X = Cl, Br, I) (44, 45).

G. The Non-Transition Metals

Apparently due to the relatively poor donor ability of PDA toward metal ions in which d_π -d_π bonding is not possible, few examples of non-transition metal complexes of PDA have been reported.

Among several non-transition metal tetra-halides tried, including UCl_4 (46), $ThCl_4$, $SiCl_4$, and $GeCl_4$ (14) only $SnCl_4$ was found to add PDA, forming the six-covalent derivatives, $[SnCl_4D]$ (46).

However with the group VI trihalides, PDA is reported to form five-covalent 1:1 addition compounds of the type $[MX_3D]$ (M = Bi, Sb, As, P; X = Cl, Br, I) (47, 48).

CONCLUSION

This seminar has attempted to summarize the known complexes of PDA as well as to examine the concepts of the nine-orbital rule and the electroneutrality principle.

It is hoped that the examples presented will serve to demonstrate the utility of these concepts and the valence bond theory in general in predicting the coordination numbers of complexes in which the bonding is primarily covalent.

TABLE III - $\underline{d}^0 \rightarrow \underline{d}^5$ Complexes

D=o-phenylenebis(dimethylarsine)

Compound	Configuration	Unpaired Electrons	Coord'n Number	Oxidation State	References
$[TiX_4D]$; X = Cl, Br	$\underline{d}^0$	--	6	IV	15, 13, 14
$[MX_4D_2]$; M = Ti, Zr, Hf; X=Cl, Br	$\underline{d}^0$	--	8	IV	13, 14
$[TiX_3D(H_2O]$; X=Cl, Br	$\underline{d}^1$	1	6	III	15
$[VX_4D_2]$; X = Cl, Br	$\underline{d}^1$	1	8	IV	13, 14
$[MoDBr_4]$	$\underline{d}^2$	2	6	IV	7
$[ReD_2X_4]Y$; X=Cl, Br; Y=ClO_4, X	$\underline{d}^2$	0	8	V	21
$[TcD_2Cl_4]Y$; Y = ClO_4, Cl	$\underline{d}^2$	0	8	V	22
$[CrDX_3(H_2O)]$; X = halogen	$\underline{d}^3$	3	6	III	49
$[CrD_2X_2]Y$; X=halogen, Y = ClO_4, $CrDX_4$	$\underline{d}^3$	3	6	III	49
$[CrCl_2D(H_2O)(ETOH)]Cl$	$\underline{d}^3$	3	6	III	4
$[MoD(CO)_3X_2]$; X = Br, I	$\underline{d}^4$	0	7	II	7
$[MoD_2(CO)_2X]$ X; X = Br, I	$\underline{d}^4$	0	7	II	7
$[MoD_2X_2]$; X = Cl, Br, I	$\underline{d}^4$	2	6	II	50
$[MD_2X_2]Y$; M = Re, Tc; X = Cl, Br, I; Y=ClO_4, X	$\underline{d}^4$	2	6	III	19, 20
$[FeD_2X_2]Y_2$; X=Cl, Br; Y=$FeCl_4$, ClO_4, ReO_4	$\underline{d}^4$	2	6	IV	26
$[OsD_2X_2][ClO_4]_2$; X = Cl, Br, I	$\underline{d}^4$	2	6	IV	25
$[MnDCl_2(H_2O)]ClO_4$	$\underline{d}^4$	4	5	III	18
$[MD_2X_2]$; M=Tc, Re; X = Cl, Br, I	$\underline{d}^5$	1	6	II	19, 20
$[MnD(CO)_2Br_2]$	$\underline{d}^5$	1	6	II	23
$[FeD_2X_2]Y$; X = Cl, Br; Y=ClO_4, FeX_4, Br	$\underline{d}^5$	1	6	III	3
$[RuD_2X_2]Y$; X = Cl, Br, I; Y=ClO_4, Br, $RuDX_4$	$\underline{d}^5$	1	6	III	24
$[OsD_2X_2]Y$; X = Cl, Br, I, SCN Y = Cl, Br, ClO_4	$\underline{d}^5$	1	6	III	25
$[MnD_2X_2]$; X=Cl, Br, I	$\underline{d}^5$	5	6	II	18

doubtful in light of more recent work (14)
little evidence cited in support of this structure.

TABLE IV. d^6 Complexes

Compound	Unpaired Electrons	Coord'n Number	Oxidation State	References
$[M(CO)_4D]$; M=Cr,Mo,W	0	6	0	16, 17
$[M(CO)_2D_2]$; M=Cr,Mo,W	0	6	0	16, 17
$[MnD(CO)_3I]$	0	6	I	23
$[MD_2X_2]$; M=Fe,Ru,Os X=Cl,Br,I,CNS	0	6	II	3,24,25,27
$[Fe(CO)_2DX_2]$; X=Br,I	0	6	II	28
$[RuD_2HCl]$	0	6	II	27
$[CoD_2X_2]Y$; X=Cl,Br,I,SCN Y=1/2 CoX_4,ClO_4, X	0	6	III	51, 30
$[CoD_3][ClO_4]_3$	0	6	III	4
$[CoD_2(C_2H_3O_2)_2]ClO_4$	0	6	III	4
$[RhD_2X_2]X$; X=Cl,Br,I	0	6	III	29
$[NiD_2X_2][ClO_4]_2$; X=Cl,Br	0	6	IV	33
$[MD_2X_2]Y_2$; M=Pd,Pt X=Cl,Br,I Y=ClO_4, NO_3	0	6	IV	34

TABLE V. d^7 Complexes

Compound	Unpaired Electrons	Coord'n Number	Oxidation State	References
$[Mn(CO)_3D]_n$ n = 1,2	1	5	0	23
$[Fe(CO)_2DI]$	1	5	I	28
$[CoD_2]Y_2$ Y=Cl,Br,I,CNS	1	4	II	51
$[CoD_3][ClO_4]_2$	1	6	II	4
$[NiD_2X_2]Y$ X=Cl,Br,SCN Y=X,ClO_4, 1/2 $PtCl_6$	1	6	III	31,32
$[NiDBr_3]$		5	III	34

TABLE VI - d^8 Complexes

Compound	Unpaired Electrons	Coord'n Number	Oxidation State	References
$NiD_3][ClO_4]_2$	0	6	II	31
$AuD_2X_2]Y$ X=Br,I; Y=ClO_4,I	0	6	III	42
$Fe(CO)D_2]$	0	5	0	28,16
$Fe(CO)_3D]$	0	5	0	28,16
$MD_2X]Y$ M=Ni,Pd,Pt;X=Cl,Br,I, NO_2,NO_3,CNS;Y=ClO_4,X	0	5	II	8,34,35
$NiD_2ClO_4]Y$ Y=ClO_4,PF_6	0	5	II	52,12
$AuD_2X]Y_2$ X=Br,I; Y=ClO_4,I	0	5	III	42
$NiD_2]X_2$ X=Cl,Br,I,CNS,	0	4	II	31,32
$NiDX_2]$ X=I,Br	0	4	II	38,34
$PdDCl_2]$	0	4	II	2
$PdD_2]Y_2$ Y=Cl, 1/2 $PdCl_4$	0	4	II	2
$MD_2][ClO_4]_2$ M=Ni,Pd,Pt	0	4	II	31,8,34
$AuD_2][ClO_4]_3$	0	4	III	42

Little evidence cited in support of these structures
Doubtful in light of more recent work (34).

TABLE VII - d^{10} Complexes

Compound	Unpaired Electrons	Coord'n Number	Oxidation State	References
$[NiD_2]$	0	4	0	39, 28
$[PdD_2]$	0	4	0	39
$[PdD(o\text{-}C_6H_4(PEt_2)_2]$	0	4	0	39
$[Ni(CO)_2D]$	0	4	0	38,5
$[CuD_2]Y$ $Y=ClO_4, CuX_2, Cl, Br, I$ $X=Cl, Br, I$	0	4	I	40
$[AuD_2]Y$ $Y=Br, I, ClO_4$, picrate, AuI_2, CuI_2	0	4	I	41,42,43
$[AgD_2]Y$ $Y=AgX_2, ClO_4$ $X=Cl, Br, I, NO_2$	0	4	I	44
$[MDX_2]$ $M=Zn, Cd, Hg$ $X=Cl, Br, I$	0	4	II	44,45
$[MD_2][ClO_4]_2$ $M=Zn, Cd, Hg$	0	4	II	44,45

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THE ZERO-VALENT COMPLEXES OF PLATINUM

L. Jane Park December 11, 1962

Studies of possible zero-valent platinum complexes did not proceed with any rapidity until about 1950. Previously, the only interest indicated was a cursory observation of the reaction of $K_2Pt(CN)_4$ with potassium metal in liquid ammonia, the product being apparently $K_4Pt(CN)_4$ (1). As recently as 1961, Nyholm and co-workers demonstrated that the compound $[(\emptyset_3P)_4Pt]$ was actually a hydride of bivalent platinum, $[(\emptyset_3P)_4PtH_2]$ (2). They then questioned the existence of any platinum(0) complex. Their work was followed, shortly thereafter, by the preparation of a compound which gave quite good evidence of being zero-valent.

This seminar will attempt to present the evidence for and against the existence of such compounds and to organize the data which has been published.

PREPARATION.

It might be expected that the zero-valent platinum compounds could be prepared by allowing the ligand to react with metallic platinum, analogously to the preparation of $Ni(CO)_4$. This, however, is not the case. In all of the cases observed, the starting material contained platinum in some oxidation state greater than zero, the most common being two. The platinum compound, usually a complex, is allowed to react with a reducing agent. Depending upon the particular reaction, a ligand may or may not be added.

Examples of the above are:

$$K_2Pt(CN)_4 + 2K \xrightarrow{NH_3} K_4Pt(CN)_4 \quad (1)$$

$$Pt(\emptyset_2PCH_2CH_2P\emptyset_2)_2\,Cl_2 \xrightarrow{NaBH_4} [Pt(\emptyset_2PCH_2CH_2P\emptyset_2)_2] \quad (3)$$

$$\underline{cis}\text{-}Cl_2[(\underline{p}\text{-}F\emptyset)_3P]_2Pt \xrightarrow{N_2H_4} [(\underline{p}\text{-}F\emptyset)_3P]_3Pt \quad (4)$$

The compound $[Pt(NS)_4]$ has been prepared from H_2PtCl_6 and $_4N_4$ (5), and its structure determined by x-ray (6). As there have een formed both $[Ni(CO)_4]$ and $[Ni(NS)_4]$, one might expect to form $Pt(CO)_4]$. Although various partially carbonyl-substituted complexes ave been prepared, e.g. $Pt(CO)[(p\text{-}Cl\emptyset)_3P]_2$ (7), no pure platinum arbonyl has been isolated. Carbonyl insertion reactions of a methyl latinum complex do not result in a zero-valent platinum complex (8).

Watt and his co-workers have prepared complexes of platinum(0) ontaining ammonia and ethylenediamine (9,10). Both are obtained by eduction of the corresponding platinum complex ion in liquid ammonia. n the preparation of $[Pten_2]$, there are a number of other complexes ormed as by-products.

The formation of platinum(0) complexes has been studied polarographically (11). Since $[Ni(CN)_4]^{=}$ has been reduced to $[Ni(CN)_4]^{4-}$ rather than to the metal, and since Pt^{++} has the same outer electron configuration as Ni^{++}, it is to be expected that $[Pt(CN)_4]^{4-}$ can be produced in this manner. Apparently, this experiment has not been attempted.

The reaction of cis-$[(P\emptyset_3)_2PtCl_2]$ with acetylene produces $[Pt(P\emptyset_3)_2ac]$ (12). Inasmuch as the acetylide ion carries a (-1) charge, the complex might be expected to contain formally univalent platinum. However, the reaction of $[Pt(P\emptyset_3)o\text{-}C_6H_4(AsMe_2)_2]$ with $C_2(p\text{-}NO_2\emptyset)_2$ produces $Pt(P\emptyset_3)_2C_2(p\text{-}NO_2\emptyset)_2$, which might be considered to contain platinum(0).

STABILIZATION OF THE ZERO-VALENT PLATINUM COMPLEXES.

The factors that lead to stabilization of the platinum(0) complexes can be applied to any compound in which the metal is in an abnormally low valence state.

Generally, one expects these complexes to comply with the Effective Atomic Number (E. A. N.) Rule. Thus, the sum of the electrons in platinum and those contributed by the ligand would be 86, corresponding to the radon configuration. An example of this is $[Pt(\emptyset_2PCH_2CH_2P\emptyset_2)_2]$. However, one would not put complete reliance on this rule to determine which compounds will be stable. Cases have been found in which the complexes contain electrons in excess of the rare-gas number, and also there is no account taken of the spatial requirements (7).

The π-bonding dative effect appears to play a large part in the stabilization, by highly electronegative atoms, of the low valence state. The π-type orbitals on the ligand must be vacant for this to occur. The metal electrons of the metal can then be fed into the ligand orbitals. This favors the donation of the ligand electrons to the metal by means of a sigma bond.

It is interesting to note that a ligand such as $[o\text{-}C_6H_4(AsMe_2)_2]$ forms platinum(0) complexes, but will stabilize abnormally high valence states as well. Filling the π-bonding orbitals of a ligand would effectively cause it to stabilize a high oxidation state.

COORDINATION NUMBER.

The coordination number of the platinum zero-valent complexes most often found is four. This complies with the E. A. N. rule. There appear to be, however, examples of coordination number other than four. If $K_2Pt(CN)_4$ is allowed to react with a potassium acetylide, (KC_2R), in liquid ammonia containing metallic potassium, there is formed a complex which analyzes as $K_2Pt(C{\equiv}CR)_2$ (13). Assuming a negative charge on the hydrocarbon donor portion, the platinum has, at least formally, an oxidation state of zero.

Coordination number three is believed to occur in several platinum zero complexes. For example, the reaction of $[(\underline{p}\text{-Cl}\emptyset)_3P]_2PtI_2$ with N_2H_4 produces $Pt[P(\underline{p}\text{-Cl}\emptyset)_3]_3$ (14). The analogous fluoro compound has also been prepared (4). Apparently three halogen-substituted phenyl phosphines are sufficient to stabilize zero valent platinum, for no tetrakis derivatives have been found.

SPECTRAL STUDIES.

Various spectrophotometric techniques have been employed to determine the actual composition of platinum(0) complexes. It has been reported that upon the addition of K_2PtCl_4 to a solution of $\emptyset_3P$ in alcohol, $[Pt(P\emptyset_3)_4]$ forms (15). However, the infrared spectrum shows bands which appear to be characteristic of the M-H stretch in metal hydrides; hence the compound is probably $[(P\emptyset_3)_4PtH_2]$ and does not contain zero-valent platinum (2).

A spectrophotometric study of the amount of bromine consumed by the reaction $[(P\emptyset_3)_4PtH_2] + 2Br_2 \rightarrow (P\emptyset_3)_4PtBr_2 + 2HBr$ indicated two hydride ions in the coordination sphere.

Spectral studies have been used also to confirm the existence of a platinum(0) complex. Infrared and nuclear magnetic resonance spectra show no Pt-H bonds in $[Pt(\emptyset_2PCH_2CH_2P\emptyset_2)_2]$ (3).

ANALOGOUS COMPOUNDS.

Inasmuch as platinum and palladium are in successive rows in the periodic table, it might be expected that the two metals would exhibit a great deal of similarity in the compounds which they form. This is found generally to be true. There are, however, some exceptions.

As was stated above, the supposed $[Pt(P\emptyset_3)_4]$ was found to be $[(P\emptyset_3)_4PtH_2]$. The compound $[Pd(P\emptyset_3)_4]$ has been produced from $C_5H_5Pd\ C_6H_9$ and $P\emptyset_3$, and no evidence is given for the possibility of hydride formation (16).

Two- and three-coordinate palladium complexes have been observed. The two-coordinate ones include the isonitriles, $[Pd(\emptyset NC)_2]$ (17). The palladium compound, $[(\underline{p}\text{-Cl}\emptyset_3P]_3Pd$, is quite analogous to the platinum compound (17).

The compound $K_4Pd(CN)_4$ is known to exist and is apparently more stable than the platinum analog (1). Experiments are hampered by the insolubility of the platinum complex.

A very interesting series of palladium compounds has been formed with ditertiary and tritertiary phosphines and ditertiary arsines (18). A novel type of isomerism appears when the ligand is a tritertiary phosphine. This arises from the number of phosphorus atoms coordinated to the platinum. The two types of ligands may be mixed in the complex. No evidence is found for metal-hydrogen bonding.

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CHELATE STABILITY AND SUBSTITUTION ON AROMATIC LIGANDS

E. J. Olszewski December 18, 1962

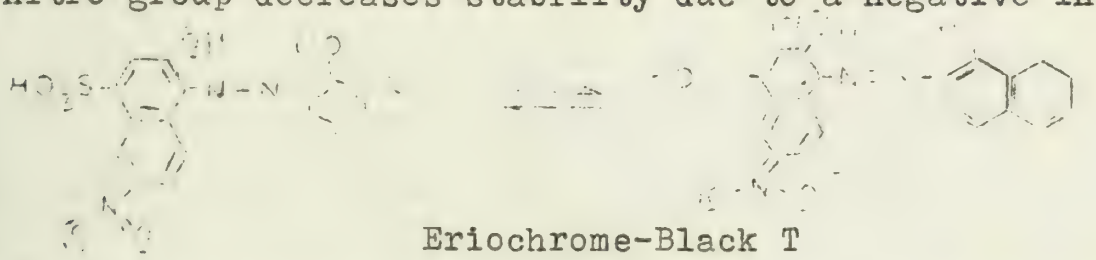
INTRODUCTION

As early as 1945, Calvin and Wilson(1) noted that no attempt had as yet been made to determine how the structural features of organic ligands could influence their tendency to form stable chelate compounds. Tate and Jones(2) have proposed a theoretical expression for the difference in stability for a pair of chelate complexes of the same metal ion having related but slightly different ligands. Martell and Calvin(3) cite inductive and steric effects and resonance interactions as the important factors involved when considering changes in chelate stability due to substitution of differing functional groups on aromatic ligands.

Tables of stability constant data have appeared as late as 1960 (4-7), but the majority of the publications dealing with this problem have appeared in the last two years. Previous to this, stability values of a specific class of aromatic ligands had to be obtained from varied sources. Thus, differences in temperature at which values were obtained or variations in solvent and in ionic strength allowed only for very general conclusions, and when different metal ions were used, for none at all.

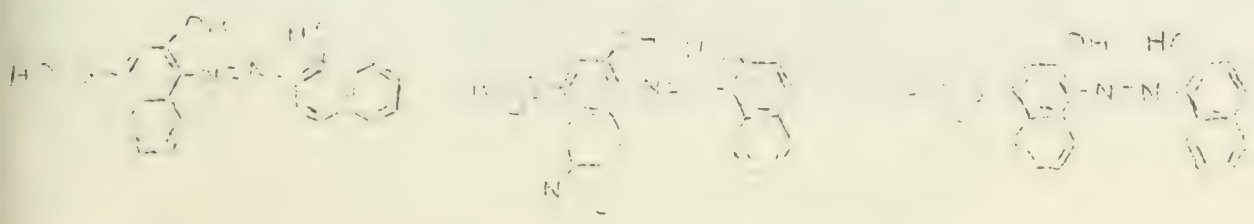
DYES

A simple illustration of the relationship between stability and ring substitution can be seen by comparing Eriochrome-Black T with Eriochrome-Black B(8). Addition of a nitro group decreases stability due to a negative inductive



Eriochrome-Black T

effect. Withdrawal of electron density from the coordinating hydroxyl oxygen is borne out by the lower stability values for both calcium and magnesium ions. For Eriochrome-Black A *versus* Eriochrome-Black R the same consideration of induction maintains, so that the lower log K_1 value for the divalent magnesium chelate of the former seems reasonable.



Eriochrome-Black B Eriochrome-Black A Eriochrome-Black R

Snavely, Fernelius, and Block(9) studied the chelate complexes of four pyrazolone dyes and found a direct relationship between the acid strength of the ligand and its power of coordination.

KETO-IMINES

Martin and co-workers(10) have discussed the stability of chelates of β-ketoimines and beryllium ion. The p-nitro group, as a result of its tendency to withdraw electrons, would increase electron density on the nitrogen by the following mechanism:

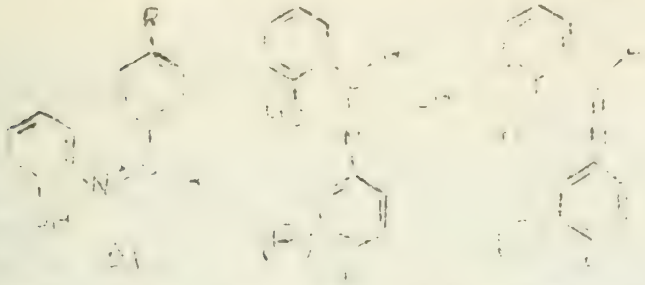
An electron donating group, such as Cl, also increases the electron density about the nitrogen atom with similar results:

Gould(11) postulates a positive resonance effect for the methoxy group, and a negative inductive influence. Thus the increase in stability of the ortho-methoxy substituted compound would be a natural consequence of resonance enhancement. In the 2,6-dimethyl substituent, steric effects decrease stability significantly. The p-methyl substituent appears as an anomaly. Having both positive inductive and resonance effects (due to hyperconjugation), it is still less stable than the unsubstituted compound.

QUINOLINES

Individual reports (12-19) had to be consulted for data on the derivatives of 8-hydroxyquinoline. Comparisons were difficult because of differences in ionic strength. The zinc(II) and magnesium(II) complexes of the 5-sulfonates are clearly less stable than those of the unsubstituted system. The negative inductive effect of the sulfonate group decreases electron density at the coordination center. Stability is increased by the 5-methyl substituent as a result of hyperconjugation. The same influence is extant in the 6-methylquinoline, but here there is no resonance interaction and as a consequence stability is not enhanced as greatly. Steric hindrance accounts for the lessened stability of the 7-methylquinoline compound, and the same reasoning applies to the 2-methyl substituent. The 4-methyl substitution increases electron density on the nitrogen atom as a result of resonance interaction making the Cu(II), Mg(II), Zn(II), and UO_2(II) chelates more stable. Additional work on the effects of quinoline substitution is reported by Yasuda(20).

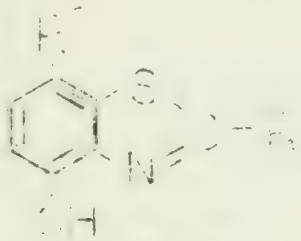
Lane and Kandathil(21) considered the series of compounds:



R = H, CH_3, OCH_3, OH

where A is a structural analog of 8-hydroxyquinoline with the same chelating system, -O-C=C-N=, except that the nitrogen atom is not part of a ring. B and C form larger chelate rings, and the effect of an <u>ortho</u> substituent can be observed. The effect of the electron donating groups is not as significant in A as in B and C. In all cases stability is increased, as demonstrated by the log <u>K</u> values. The large increase in stability of C over B is possibly due to an increase in entropy caused by the blocking effect of the methoxy group in the 3-position. The electron donating influence of the 3-methoxy group is also a factor.

The 4-hydroxybenzothiazoles are also similar to the 8-hydroxyquinolines (22).



R = H, NH_2, $NHCH_3$

R' = H, CH_3

The values obtained for the formation constants of the metal chelates of 2-amino-4-hydroxybenzothiazole, 2-methylamino-4-hydroxybenzothiazole, and 7-methyl-2-amino-4-hydroxybenzothiazole are higher than those obtained with the corresponding metal chelates of 4-hydroxybenzothiazole. The increase in stability is attributed to the increase of electron density in all cases at the centers of coordination. The metal species considered were Cu(II), Pb(II), Ni(II), Zn(II), Co(II), and Cd(II).

Feng and Fernando(23) studied some additional derivatives of this class of ligand. They used as metal species divalent zinc, cadmium, nickel, cobalt, and manganese. Their results supported those of Lane and Sam(22), and in addition they examined 5,7-dibromo-4-hydroxybenzothiazole and 4-hydroxybenzothiazole-7-sulfonate. For the former ligand, stability was diminished as a consequence of the negative inductive effect of the bromine pair. However, the 7-sulfonate derivative gave results which could not be explained.

SALICYLALDEHYDES

Work has been done on many of the divalent copper derivatives of salicylaldehydes(24,25). The 3-ethoxy and 3-propyl substituents both increase stability. The steric factor does not seem to be operative here. Increased stability is observed for the 4-methoxy species also, but unlike the 3-ethoxy derivative, lack of resonance interaction diminishes its effectiveness. Small stabilization occurs with the 4-methyl, but more significantly with the 3,5-dimethyl where hyperconjugation can be more greatly felt in addition to the positive inductive effect. The negative inductive effect of the 5-sulfonate lessens the log β_2 as do both the 3- and 4-nitrosalicylaldehydes.

The strong -I effect of fluorine accounts for the lower stability of the 3-fluoro derivative. In the 3- and 5-chloro compounds a competition exists between the -I and +R effects. The lower log β_2 value for the 3-chloro analog is due to the favored inductive effect of the closer chloride.

Jones and co-workers(26) studied the nitro-, chloro-, and methoxy- substituents each on the positions ortho, meta, and para to the OH group. The nitro group weakens stability the greatest in the ortho position whereas the chelate of the m-nitro is the most stable of the three as a result of negligible resonance interaction. For both the chloro and methoxy derivatives, the meta position again gives the most stable species, which is completely unexpected because of the unfavorable resonance interaction.

SALICYLATES

Of the salicylic acid type chelates, the iron(III) derivatives of the 5-sulfo and 5-amino species have been examined(27,28). The stability values decrease for the sulfo species and increase with the amino group. The negative inductive effect of the latter is not so effective due to its distance from the coordination center. Foye and Turcotte(29) in a more recent work reported similar results and extended their study of the 4-amino compound in addition to various nitro, chloro, and alkyl derivatives. They reported small variations in stability constants among the alkyl derivatives but stabilities which were generally slightly higher than that for the parent compound. The 5-chloro species gave slightly lower values whereas the greatest decrease in stability was found for the 3- and 5-nitro species. Tervalent iron and aluminum were the metal ions involved.

ANTHRANILATES

Harris and Sweet(30) considered the divalent copper and cadmium chelates of 5-sulfo, 3,5-diiodo, and 3-methyl anthranilic acids. Stability constant values varied slightly from those of the unsubstituted chelate, and the tendency was toward decreasing stability resulting from steric interaction. The work was expanded by Young and Sweet(31), who studied bulkier derivatives of anthranilic acid and attributed the decrease in stability to steric interactions.

PHENOLS

Sims(32) and Perrin(33) compared the stabilities of 3-hydroxyanthranilic acid and o-aminophenol chelates. For Mn(II), Fe(II), Co(II), Ni(II), and Cu(II), Sims found the o-aminophenolates to be more stable in all cases. Perrin studied just the iron ion and found the opposite to be true. The 3-amino-4-hydroxybenzenesulfonic acid gave less stable iron(II) chelates than the o-aminophenol because of withdrawal of electron density by the sulfo group.

The 2-nitrosophenol chelates of divalent cobalt and copper were studied by Shimura(34). The trend in stability is given as 5-CH_3>5-OCH_3>4-CH_3>Nph, 4-Cl>4-Br. He also found the 4-methyl derivative to be consistently more stable than the 4-chloro for the divalent copper, nickel, lead, zinc, and cadmium ions.

AMINES

Silver complexes of aniline derivatives (35,36) comprise the next class of ligands. The negative inductive effect of the meta-nitro group diminishes log β_2 from 3.17 (for aniline) to 1.7. The additional factor of resonance enables the para-nitro constituent to cause even greater lowering of log β_2 to 1.6.

Positive inductive effects exert a stabilizing influence in all cases of substitution by methyl groups. The order of stability here is para>ortho>meta, with log K_1 values of 1.56, 1.51, and 1.47 respectively. The disubstituted methyl anilines give even more stable chelates.

Fyfe(37) compared the stability of aniline complexes of silver(I) with those of ortho-, meta-, and para-substituted toluidine, bromoaniline, chloroaniline, and nitroaniline. Stability was enhanced for the toluidines but lowered for the last three classes.

Armeanu and Luca(38) reported that the stability of complex silver ions was increased by the introduction of the methyl group into the aromatic aniline nucleus, and lowered by

substitution of -Cl, $-NO_2$, and -I. The authors claimed that the lower stability of the complex ions formed with o-toluidine and dimethyl-o-toluidine supported the hypothesis that the lower basicity of the methyl-o-toluidines has its cause in steric hindrance.

In ortho, meta, and para amine-substituted pyridine compounds (35,39-43) stability is increased. The para substituent produces the greatest stability whereas the steric factor at the ortho position and the poor resonance interaction meta account for their less stable silver(I) complexes.

The positive resonance and inductive effects of the methyl group explain the stability increase of the o-, m-, and p-pyridine derivatives.. The effect of hyperconjugation by $-CH_3$ groups is not as great as the resonance interaction of $-NH_2$; thus the pyridyl amine chelates are the more stable. The three methyl groups of 2,4,6-trimethylpyridine cause an even greater increase in stability, but the 2,4-dimethyl member of the series gives the most stable chelates because of reduced steric hindrance.

Both resonance interaction and inductive influence are negative for the -CN group, explaining the lessened stability of these pyridyls.

For the nicotinamides and the methyl nicotinates there is a stability decrease, with the para compounds proving the least stable. The para position is more effective than the meta in raising the stability when the methoxy substituent is introduced.

Divalent cobalt, copper, and nickel complexes of picolinic acid and its 6-methyl derivative have been examined. The lower log K values for the metal chelates of the latter derivative is attributed to a steric factor.

DIPYRIDYLS

Chelate stability decreases in the case of both 5-chloro and 5-nitro substitution on the dipyridyls(44-46). Little change is observed in the 5-phenyl derivative, while with the 5-methyl substituent stability is increased. The log B_2 value of 7.9 for the 2-methyl iron(II) species is extremely low and is an example of the destabilizing effects of steric interaction. This effect is multiplied for the 2,2'-disubstituted dipyridyls (47), and a similar destabilization is found to occur for the 5,5'-disubstituted species by preventing the aromatic rings in the ligand from assuming a coplanar configuration (48).

OTHER LIGANDS

Singh and Banerjee(49) studied a group of violuric acids and found that the introduction of a methyl group in the side benzene ring enhances the stability of the metal chelates. The

effect of the methyl group is most pronounced when it is situated in the meta position and is less when it is in the para position. The low stability of the ortho-methyl chelate is attributed to steric hindrance.

Schwarzenbach and co-workers(50) and Calvin and Bailes(51) have reported studies on a number of metals forming chelates with variously substituted sulfonates and carboxylates of anilinediacetic acid.

In studying a number of related drugs, Andrews et al (52) have remarked that whereas only slight differences in chelate stability were noted, the resulting differences in physiological effects were considerable.

Tate and Jones(2) wanted to determine the usefulness of the Hammett equation to correlate stability constants of cadmium complexes for over twenty substituted benzenesulfonates. They concluded that structural parameters other than those used to represent inductive effects would be required. However they also noted that very few of the expected changes were found as substituents were varied from electron withdrawing to electron donating. They also reported no consistent obvious evidence of steric hindrance arising from ortho substitution.

CONCLUSION

Generally substitution effects on aromatic ligands will correspond with results predicted from theory. In only half of the cases studied is a linear relationship to be found between ligand basicity and chelate stability. A consideration of the relationship between ligand substitution and reaction rates would be a logical extension of this paper. Also interesting would be a study of ligand substitution effects on the oxidation potential of the metal chelates.

TABLE I

β-Ketoimines(10)

$CH_3COCH_2C(=NR')CH_3$

M = Be(II), Temp. = 30°C., Ionic Strength = 50% dioxane

Ligand: R' =	log K_1	log K_2	log β_2
Phenyl	10.87	10.49	21.36
4-Nitrophenyl	12.04	10.63	22.67
2-Methoxyphenyl	10.90	10.63	21.53
2,6-Dimethylphenyl	9.98	10.30	20.28
4-Chlorophenyl	11.47	10.75	22.22
4-Methylphenyl	10.43	10.61	21.04

TABLE II

8-Hydroxy Quinolines

Substituted Ligand	Divalent Metal	t	Ionic Strength	log K_1	log K_2	log β_2	Reference
	Cu	25°	50% dioxane	13.49	12.73	26.22	12
	"	20°	0.01	12.20	11.20	23.40	13
	"	25°	70% dioxane	15.00	14.00	29.00	14
8-Hydroxy-Quinoline	"	20°	50% dioxane 0.3M $NaClO_4$	13.03	12.35	25.38	15
	Mg	25°	50% dioxane	6.38	5.43	11.81	12
	"	25°	70% dioxane	6.88	5.96	12.84	14
	"	20°	50% dioxane 0.3M $NaClO_4$	5.04	4.29	9.33	16
	Zn	25°	50% dioxane	9.96	8.90	18.86	12
	"	25°	70% dioxane	10.91	9.90	20.81	14
	"	20°	50% dioxane 0.3M $NaClO_4$	9.34	8.22	17.56	15
	UO_2	20°	"	11.25	9.64	20.89	15
	Cu	25°	→ 0	11.53	10.1	21.6	17
	"	20°	~0.01	12.5	10.6	23.1	13
	"	25°	~"	11.5	10.7	22.2	18
5-Sulfo	Mg	25°	→ 0	4.79	3.4	8.2	17
	"	20°	~0.01	4.8	3.7	8.5	13
	Zn	25°	→ 0	8.65	7.5	16.2	17
	"	20°	~0.01	8.4	6.7	15.1	13
	"	25°	~"	8.7	7.2	15.7	18
	Cu	20°	50% dioxane 0.3M $NaClO_4$	13.55	12.35	25.90	15
5-Methyl	Mg	"	"	5.21	4.47	9.68	"
	Zn	"	"	9.46	8.40	17.86	"
	UO_2	"	"	11.25	9.52	20.77	"
6-Methyl	Mg	"	"	5.09	4.31	9.40	"
	UO_2	"	"	10.89	9.26	20.15	"
	Mg	"	"	4.64	4.12	8.76	"
7-Methyl	UO_2	"	"	11.28	9.78	21.06	"
	Zn	"	"	9.31	8.11	17.42	"
	Cu	25°	50% dioxane		13.52		19
4-Methyl	Mg	"	"	6.45	5.46	11.91	"
	Zn	"	"	10.67	9.57	20.24	"
	Cu	20°	50% dioxane 0.3M $NaClO_4$	12.48	11.52	23.80	"
		25°	50% dioxane	10.22	9.32	19.54	"
2-Methyl	Mg	20°	50% dioxane 0.3M $NaClO_4$	5.24	4.48	9.72	"
		25°	50% dioxane	3.73	3.13	6.86	"
	Zn	20°	50% dioxane 0.3M $NaClO_4$	8.66	8.10	16.76	"
	UO_2	"	"	~9.4	8	17.4	"

TABLE III

4-Hydroxybenzothiazoles(22)

Temp. = 25°C., Ionic Strength = 50% dioxane

	4-Hydroxybenzothiazole			2-Amino-4-Hydroxybenzothiazole		
	log K_1	log K_2	2 log $K_{av.}$	log K_1	log K_2	2 log $K_{av.}$
Cu(II)	9.0	8.0	17.1		9.8	21.1
Pb(II)	7.7	5.0	12.5	9.0	6.3	15.1
Ni(II)	7.3		13.5	8.0		
Zr(II)	6.7			8.0		
Co(II)	7.1			7.6	6.6	14.3
Cd(II)	6.9		12.3	7.9	6.1	14.2

	2-Methylamino-4-Hydroxy-Benzothiazole			2-Amino-4-Hydroxy-7 Methylbenzo-thiazole		
	log K_1	log K_2	2 log $K_{av.}$	log K_1	log K_2	2 log $K_{av.}$
Cu(II)	10.9		21.3	11.5	10.5	21.7
Pb(II)	9.8	(9.0)	17.8	9.5	6.9	16.4
Zn(II)	8.3	7.9	16.2	8.5		(16.4)
Ni(II)	8.3	7.4	15.7	8.6	7.6	16.2
Co(II)				8.2	7.1	15.2
Cd(II)				8.2	7.0	15.1

TABLE IV

4-Hydroxybenzothiazoles(23)

Temp. = 25°C., Ionic Strength = 50% dioxane, 0.1 M NaCl

	4-Hydroxybenzothiazole		2-Amino-4-Hydroxybenzothiazole	
	log K_1	log K_2	log K_1	log K_2
Zn(II)	6.90	5.92	8.0	7.4
Cu(II)	9.28	8.15	11.4	10.5
Ni(II)	7.35	6.11	8.1	7.2
Co(II)	6.88	6.60	7.8	6.8
Mn(II)	5.36	4.88	6.2	5.2

	4-Hydroxybenzothiazole--7-Sulfonic Acid		5,7-Dibromo-4-Hydroxybenzothiazole
	log K_1	log K_2	log K_1
Zn(II)	6.1	4.3	
Cu(II)	9.5	7.8	7.1
Ni(II)	8.1	5.9	5.4
Co(II)	7.9	5.8	4.9
Mn(II)	5.1	3.9	

TABLE V

Salicyladehydes

M=Cu(II)

Substituted Ligand	t	Ionic Strength	log β_2	Reference
Salicylaldehyde	25°C	50% dioxane	13.31	24
3-Propyl	20°C	50% dioxane $\simeq$ 0.1	14.2	1
3-Ethoxy	20°C	50% dioxane $\simeq$ 0.1	14.2	1
4,6-Dimethyl	20°C	50% dioxane $\simeq$ 0.1	14.4	1
4-Methoxy	20°C	50% dioxane $\simeq$ 0.1	13.8	1
5-Methyl	20°C	50% dioxane $\simeq$ 0.1	13.4	1
5-Nitro	20°C	50% dioxane $\simeq$ 0.1	8.8	1
4-Nitro	20°C	50% dioxane $\simeq$ 0.1	9.2	1
3-Nitro	20°C	50% dioxane $\simeq$ 0.1	8.2	1
5-Sulfo	25°C 40°C	$\simeq$ 0.2 $\simeq$ 0.2	9.27 9.79	27 27
3-Floro	20°C	50% dioxane $\simeq$ 0.1	11.4	1
5-Chloro	20°C	50% dioxane $\simeq$ 0.1	11.4	1
3-Chloro	20°C	50% dioxane $\simeq$ 0.1	10.6	1

TABLE VI

Salicylates (29)

Temp. = 20°C., Ionic Strength = 95% ethanol

	Fe(III)			Al(III)		
	log K_1	log K_2	log K_5	log K_1	log K_2	log K_5
4-amino-	16.30	13.91	30.48	15.57	12.45	28.02
4-methyl-	16.26	11.89	29.84	15.76	11.65	27.41
3,5-diisopropyl-	16.23	11.59	29.66	15.62	11.75	27.37
5-tert-butyl-	16.06	12.21	29.44	15.60	11.56	27.16
Salicylic Acid	16.53	12.69	29.34	15.62	11.45	27.07
3-isopropyl-6-methyl-	16.03	11.34	29.08	15.45	11.50	26.95
3-methyl-	15.99	11.85	29.04	15.26	11.53	26.79
5-chloro-	16.07	12.82	28.96	16.02	11.73	27.75
3-nitro-	14.60	12.46	27.54	14.25	11.85	26.10
5-nitro	14.51	12.67	26.86	14.31	12.16	26.47

TABLE VII

Anthranilates(30)

	Divalent Metal	$K_1 \times 10^{-4}$
3-methylanthranilic acid	Cd	0.32
	Cu	7.9
N-methylanthranilic acid	Cd	0.30
	Cu	3.7
Anthranilic acid	Cd	0.16
	Cu	14
5-sulfoanthranilic acid	Cd	0.26
	Cu	8.7
N-phenylanthranilic acid	Cd	0.21
	Cu	0.63
3,5-diiodoanthranilic acid	Cd	0.05
	Cu	0.45

TABLE VIII

Phenols(32)

			Ni(II)		Co(II)	Cd(II)	Mn(II)
Ligand	pK_a	pK_a	K_1	K_2	K_1	K_1	K_1
-Hydroxyanthranilic Acid	10.09	5.20	5.1	3.6	4.4	4.3	3.4
-Amino-4,5-dimethyl phenol hydrochloride	10.40	5.28	5.9	4.8	5.3	4.9	3.6
-Aminophenolhydrochloride	9.99	4.86	5.4	-	4.7	4.3	3.6

continued

Phenols (33)

	Mn(II)	Fe(II)	Co(II)	Ni(II)	Cu(II)
3-Hydroxyanthranilic acid	3.4	7.7	4.4	5.1	-
O-aminophenol	3.6	8.0	4.7	5.4	8.8

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		log K_1	log β_2	Ionic Strength
O-aminophenol	Fe(II)	3.66	6.34	0.006
	Cu(II)	8.77	16.14	0.002
3-amino-4-hydroxy-benzenesulfonic acid	Fe(II)	3.32	6.13	0.009
3-Hydroxyanthranilic acid	Fe(II)	3.8	8.3	0.002
4-amino-5-hydroxy naphthalene-2,7-disulfonic acid (monosodium salt)	Fe(II)	2.57	5.5	0.018
	Cu(II)	6.91	11.15	0.020

TABLE IX

Anilines

Temp = 25°C., M = Ag(I)

Ligand	Ionic Strength	log K_1	log β_2	Reference
Aniline	1M KNO_3	1.44		36
	50% mol. C_2H_5OH		3.17	35
m-nitroaniline	"		1.7	"
p-nitroaniline	"		1.6	"
o-methylaniline	"		3.17	"
"	1M KNO_3	1.51		36
m-methylaniline	"	1.47		"
p-methylaniline	"	1.56		"
"	50% mol. C_2H_5OH		3.48	35
3,5-dimethylaniline	1M KNO_3	1.63		36
2,6-dimethylaniline	"	1.62		

Anilines(37)

M = Ag(I), Temp.=25°C., Ionic Strength= 59% Wt. ethanol-H_2O

Ligand	log Kf	Ligand	log K_f
Aniline	3.0		
O-Toluidine	3.65	O-chloroaniline	2.5
m-Toluidine	3.4	m-chloroaniline	2.55
p-Toluidine	3.9	p-chloroaniline	2.5
o-Bromoaniline	2.8	o-nitroaniline	1.9
m-Bromoaniline	2.8	m-nitroaniline	1.7
p-Bromoaniline	2.75	p-nitroaniline	1.7

TABLE X

Pyridines

Temp. = 25°C. M = Ag(I)

Ligand	Ionic Strength	log K_1	log K_2	log β_2	Reference
Pyridine	→ 0	1.97	2.38	4.35	39
"	→ 0			3.82	40
"	0.5 KNO_3	2.04	2.18	4.22	41
"	50% mol. C_2H_5OH			3.88	35
-aminopyridine	?	2.86	2.89	5.75	42
-aminopyridine	?	2.17	3.04	5.21	"
-aminopyridine	?	2.80	3.40	6.20	"
-methylpyridine	0.5M KNO_3	2.27	2.41	4.68	41
-methyl pyridine	→ 0	2.00	2.35	4.35	39
-methyl pyridine	0.5M KNO_3	2.24	2.46	4.70	41
"	→ 0	2.03	2.36	4.39	"
-cyanopyridine	"			2.90	39
-cyanopyridine	"			3.08	"
,4,6-dimethylpyridine	50% mol. C_2H_5OH			4.75	35
,4-dimethylpyridine	0.5M KNO_3	2.47	2.71	5.18	41
icotinamide	→ 0			3.22	39
iso-Nicotinamide	"			3.01	"
-methoxypyridine	"	1.58	2.09	3.67	"
-methoxypyridine	"	2.28	2.16	4.44	"
ethyl nicotinate	"			2.99	"
ethyl *iso* nicotinate	"			2.45	"

TABLE XI

Phenanthrolines

M=Fe(II)

Ligand	Temp.	Ionic Strength	log K_1	log K_2	log β_2	log K_3	log β_3	Reference
:10-phenanthroline	25°C.	→ 0			21.3			45
"	"	"			21.5			"
-Nitro-1:10-phenonthroline	"	"			17.8			46
-Chloro-1:10-phenanthroline	"	"			19.7			"
-Methyl-1:10-phenanthroline	20°C	→	4.2	3.7	7.9	2.9	10.8	47
-Methyl-1:10-phenanthroline	"	"					22.3	46
-Phenyl-1:10-phenanthroline	25°C	-			21.1			"

TABLE XII

Anilinediacetic Acids(50,51)

Temp.=20°C., Ionic Strength = 0.1

Ligand	Metal	log K_1
Anilinediacetic acid	Mg(II)	1.15
	Ca(II)	0.6
	Fe(II)	2.01
2-Hydroxyaniline diacetic acid	Fe(II)	7.69
2-Sulfoaniline diacetic acid	Mg(II)	2.68
	Ca(II)	4.57
3-Sulfoaniline diacetic acid	Mg(II)	1.26
	Ca(II)	1.26
4-Sulfoaniline diacetic acid	Mg(II)	1.15
	Ca(II)	0.95
2-Carboxyanilinediacetic acid	Mg(II)	3.91
	Ca(II)	5.06
3-Carboxyanilinediacetic acid	Mg(II)	1.38
	Ca(II)	1.46
4-Carboxyanilinediacetic acid	Mg(II)	1.30
	Ca(II)	1.30

TABLE XIII

Benzenesulfonates(2)

M=Cd(II), Temp. = 25°C.

	Ligand	K_1
1.	4-Aminobenzenesulfonate	0.1983
2.	4-Methylbenzenesulfonate	0.3604
3.	Benzenesulfonate	0.4185
4.	2-Chloroaniline-4-sulfonate	0.5451
5.	Benzene-1,3-disulfonate	0.6960
6.	4-Chlorobenzenesulfonate	0.8540
7.	4-Bromobenzenesulfonate	0.9215
8.	2,4,6-Trimethylbenzene-sulfonate	1.505
9.	2,5-Dimethylbenzenesulfonate	1.586
10.	4-Amino-3-methylbenzenesulfonate	1.743
11.	3-Aminobenzenesulfonate	1.759
12.	2-Aminophenyl-4-sulfonate	2.247
13.	2,5-Dichloro-4-aminobenzenesulfonate	2.411
14.	4-Chloro-3-methylbenzenesulfonate	2.460
15.	2,4-Dimethylbenzenesulfonate	2.700
16.	2-Hydroxy-4-methoxybenzophenone-5-sulfonate	2.748
17.	4-Hydroxybenzenesulfonate	2.822
18.	4-Toluidine-2-sulfonate	2.839

TABLE XIII (CONTINUED)

Ligand	K_1
19. 1-Methylbenzenesulfonate	3.153
20. 2-Chloroaniline-5-sulfonate	3.213
21. 1-Benzaldehydesulfonate	3.496
22. 3-Toluidine-4-sulfonate	12.76
23. 2,5-Dichlorobenzenesulfonate	13.92
24. Aniline-N-methylsulfonate	29.52

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CHEMICAL EFFECTS OF NUCLEAR TRANSFORMATIONS IN THE GAS PHASE

Agnes Chia Wang January 8, 1963

I. INTRODUCTION

The product atom from a nuclear reaction usually acquires a large momentum and often possesses kinetic and electronic energies far in excess of chemical bond energies. Such excited atoms then move through the surrounding medium while losing energy and being slowed down by collision. During these collisions, the recoil atom may undergo reaction leading to stable chemical combination. The area of "hot atom" chemistry involves the study of these chemical effects of nuclear transformations.

From certain points of view, we can classify the studies into four groups:

1. Chemistry of atoms formed by induced nuclear reactions.
   - Product isotopic with the target (Szilard-Chalmers type of reaction); for example, $C^{12}(\gamma,n)C^{11}$ and (n,γ) reactions of halogens.
   - Product non-isotopic with the target; for example, $N^{14}(n,p)C^{14}$, $He^{3}(n,p)T$ and $Li^{6}(n,\alpha)T$ reactions.

2. Chemistry of atoms formed by isomeric transition; for example, $Br^{80m} \rightarrow Br^{80}$.

3. Chemistry of atoms formed by alpha-decay; for example, the study of Pb^{212}.

4. Chemistry of atoms formed by beta-decay; for example, the study of Bi^{210} and beta-decay product of tritium.

This seminar will be limited to discussions of the gas-phase reactions only. For work in this field as well as on liquid and solid phase reactions, a number of general review articles are available. (1,2,3,4,5)

II. THEORETICAL STUDIES

Theoretical studies in this field are still in their infancy (6). A number of workers have proposed different models in an attempt to describe the mechanisms of the hot-atom reactions, such as the billiard ball model of elastic collision by Libby and coworkers (7); the Estrup-Wolfgang model (8), the simple model for competitive tritium reactions by Rowland and coworkers (9); and the mathematical model formulated by Cerdus and Hsung (10). The last authors also published calculated results concerning momentum transfer to an atom in a molecule (11), and failure to bond-rupture following nuclear recoil from (n, γ) activation (12). In all the cases, a number of assumptions have to be made.

III. EXAMPLES OF EXPERIMENTAL RESULTS

1. Halogens, Cl^{38}, Br^{80}, Br^{80m} and I^{128}

Recoil halogen atom reactions in the gas phase, $Cl^{37}(n,\gamma)Cl^{38}$ (13), $Br^{79}(n,\gamma)Br^{80}$ (14), and $I^{127}(n,\gamma)I^{128}$ (15) were studied by Willard and coworkers. They found that the recoil halogen atoms in the gaseous hydrocarbons were able to replace the hydrogen atom. The organic yields ranged from a few percent for chlorine to about 54% in the case of iodine in the presence of methane. These facts indicate that some of the halogen atoms produced by (n,γ) processes can react with a hydrocarbon chain in a one-step reaction to become organically bound.

Recent studies by Rack and Gordus of the same reactions in the presence of inert-gas moderators show that, in the case of bromine, the reaction with methane occurs principally as a result of the recoil kinetic energy acquired by the Br^{80} in the (n,γ) activation process (16). For iodine, their data suggested that of the 54.4% organic yield as a consequence of the (n,γ) activation, about 18% forms as a result of hot I^{128} reactions, 11% as a product of excited iodine atoms or I^{+} ions in the $^3P_2$, $^3P_1$, and/or $^3P_0$ states, and 25% as a result of reactions of $I^{+}(^1D_2)$ ions (17). They also reported that the manner in which molecular additions inhibit the reaction of (n,γ) activated I^{128} with CH_4 also enable them to study indirectly interactions of other molecules with atoms activated by neutron processes (18).

Willard and coworkers also studied the reactions activated by the Br^{80m} isomeric transitions (19). They found that the yields are lower than that from the (n,γ) process.

2. Carbon, C^{11} and C^{14}

C. Mackay and coworkers (20) reported the study of reactions of carbon atoms with a number of gaseous molecules using 20.5-min. C^{11} produced by a neutron stripping reaction of C^{12}. With simple oxidizing agents (e.g., air, O_2, O_2-O_3 mixtures, CO, CO_2 NO, NO_2, N_2O and SO_2) carbon monoxide is always the major product. They explained this in terms of a third body restriction on the further oxidation to CO_2. With hydrogen, the recoil carbon atom gives half methane and half CO although the only sources of oxygen are trace impurities and the wall. With hydrocarbons the most important single product in all systems is acetylene, amounting to 30-35%. From the results they were able to point to the existence of several reaction mechanisms, involving C-H, C-C bonds.

Yang and Wolf studied the $N^{14}(n,p)$ C^{14} reaction in anhydrous ammonia in the gas phase (21). A uniquely high specific yield of methane-C^{14} has been observed. This high yield of methane-C^{14} as essentially the sole significant product from operations of the recoil carbon in gaseous ammonia was not

affected by the addition of inert moderating gases. The presence of oxygen as radical scavenger did not produce any significant effects. Reaction of the recoil carbon in the presence of methane and methylamine, however, gave a complex mixture of radioactive products, which is common to all carbon-14 systems. Yang and Wolf proposed a process of hydrogen abstraction to account for the apparently unique result from the recoil carbon in the presence of ammonia in the gas phase. They also used a collision complex mechanism to account for the nature of the recoil fragments.

3. Tritium

Hot-atom chemistry of tritium in the gas phase is probably the most extensively studied branch in this field(22,23,24,25). Hot displacement was observed in alkanes in which H, 2H, or an alkyl group is displaced. The types of reactions are:

A. Hydrogen atom abstraction. This reaction, the only one observed at thermal energies, also occurs with hot hydrogen (although with a much higher collision yield)

$$T^* + RCH_2CH_3 \rightarrow \begin{matrix} RCH\cdot CH_3 \\ RCH_2CH_2\cdot \end{matrix} + HT$$

B. Hydrogen atom displacement

$$T^* + RCH_2CH_3 \rightarrow \begin{matrix} RCH_2CH_2T \\ RCHTCH_3 + H \end{matrix}$$

C. Replacement of alkyl group to form a degraded alkane

$$T^* + RCH_2CH_3 \rightarrow \begin{matrix} CH_3T \\ CH_3CH_2T \\ RCH_2CH_2T \quad \text{etc.} \end{matrix}$$

D. Replacement of two groups to form a radical. Either two hydrogen atoms or a hydrogen atom and an alkyl group may be displaced by the hot atom.

$$T^* + RCH_2CH_3 \rightarrow RCH_2CHT + H_2$$

The resulting radical may combine with iodine scavenger to form alkyl iodide. Alternatively, it may decompose into a smaller radical and an alkene by breaking a C-C bond with rearrangement,

$$CH_3CH_2CH_2CHT\cdot \rightarrow CH_3CH_2\cdot + CH_2CHT$$

The reactions initiated by beta decay of tritium forming tritiated hydrocarbons in systems initially composed of gaseous propane and tritium are also reported (26).

4. Lead-212 from α-decay

The observations that recoil tritium and halogen atoms undergo substitution reactions in the gas phase have led to an investigation with recoil metal atoms to see whether similar reactions occur. Accordingly, the gas phase reactions of lead-212 recoiling from alpha decay of polonium-216 have been studied (27,28).

These studies have indicated that the Pb^{212} produced by alpha decay in the presence of such gases as CH_4, Ar, and CO is retained in the gas phase to a large extent and may be transferred as a vapor using standard vacuum line techniques. Further studies regarding the method by which the recoil lead is retained in the vapor phase are still in progress. At the present time, it seems quite likely that aerosol formation may be at least partly responsible for the observed results.

IV. CONCLUSION

The chemical effect of nuclear transformations, or hot atom chemistry is a branch of radiochemistry that is relatively new and not well understood. Although much progress has occurred since observations by Szilard and Chalmers in 1934 (29) opened the field, more effort should be made to explore this area.

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RECENT CHEMISTRY OF THE ALANES

D. P. Eyman January 15, 1963

I. INTRODUCTION

The chemistry of the alanes [alane is the name proposed by Wiberg for aluminum hydride and its derivatives (1)]is dominated by a highly acidic character and the tendency of the aluminum to attain tetra coordination. These characteristics are demonstrated by the common occurrence of associated alanes (2,3); amine and ether adducts of alanes, which are more stable than analogous borane adducts (4); and anionic complexes with alkali metal halides and alkyls. The strength of the aluminum-nitrogen coordinate bond in amine alane adducts is such that with the correct substituents on nitrogen and aluminum condenstation to amino alanes and imino alanes is possible (5).

II. AUTOCOMPLEXATION

The large tendency for alanes to associate comes from the electron deficiency of aluminum compounds with a coordination number of three. Association leads to dimers, trimers, and polymers with atoms or groups as bridges bound by three-center bonds.

The structure of dimeric trimethylalane, as established by X-ray crystal analysis, involves bridging methyl groups (6). It has been shown that in higher trialkylalanes the α carbon of the alkyl group forms a bridge between aluminum atoms (7). The dimers have a distinct tendency to dissociate to monomers in the vapor phase at temperatures up to 160°C. The degree of association of trialkylalanes decreases in the order (8)

$$Me_3Al > Et_3Al > Pr_3Al.$$

Triisopropylalane, triisobutylalane, and all alanes of the types $Al(-CH_2CHRR')_3$ and $Al(-CH_2CR_3)_3$ are monomeric, as determined cryoscopically in benzene (2). In general the tendency to dimerize diminishes with increasing alkyl chain length or increasing alkyl complexity. This behavior is probably the result of steric hindrance (9).

Dialkylalanes are trimeric according to cryoscopic measurements in benzene (10). There is no difference among the methyl, ethyl, and isobutyl compounds. Infrared studies indicate that association occurs by way of Al-H-Al bonds. The heat of association is estimated to be 15-20 kcal. per hydrogen bridge (11).

Alanes of the type R_2AlX (R=alkyl;X=OR,NR_2,PEt_2,Cl) are associated through Al-X-Al bridges. The dimers and trimers

$$(R_2AlCl)_2 \quad (Et_2AlOEt)_2 \quad (Et_2AlNEt_2)_2 \quad (Et_2AlOMe)_2 \quad (Et_2AlPMe_2)_2$$

are known in (9,12).

Deaggragation of some of these polymers can be effected by addition of electron donors. The compounds Me_2NAlCl_2, $Me_2NAl(C_6H_5)_2$, and $Me_2NAl(C_4H_9)_2$ are inert to the attack of bases (13).

Alane "inner complexes" of the type $R_2Al(CH_2)_3Y$(R=alkyl,aryl; Y=OEt,SEt,OPr,NEt_2), as well as $R_2Al(CH_2)_4OEt$ are known (14,15,16). The thermal condensation of triphenylalane and acetylacetone produces diphenylalane acetylacetonate, which has been assigned a chelate structure (17).

III. MOLECULAR COMPLEXES

Alane and trialkylalanes behave as very strong acceptors and form complexes with ethers and amines which are more stable than the analogous borane complexes. The following order of donor character towards trimethylalane has been established (4,18).

$$Me_3N > Me_3P > Me_2O > Me_2S > Me_2Se > Me_2Te$$

Wiberg (19) has reported that triethylamine alane is largely dimeric in benzene whereas tripropylamine alane is only slightly dimerized and tributylamine alane is monomeric. All of these are monomeric in diethyl ether. The values for the degree of association (n) of some amine alane adducts in benzene are listed in Table I (20).

Table I
Degree of Association for Amine Alane Adducts

Compound	n	Compound	n
$Me_3N:AlH_3$	1.40	$Me_3N:AlHCl_2$	1.46
$AllylMe_2N:AlH_3$	1.37	$Me_3N:AlCl_3$	1.36
$Et_2MeN:AlH_3$	1.33	$Et_3N:AlH_3$	1.10
$Me_3N:AlH_2Cl$	1.32	$Pr_3N:AlH_3$	1.05

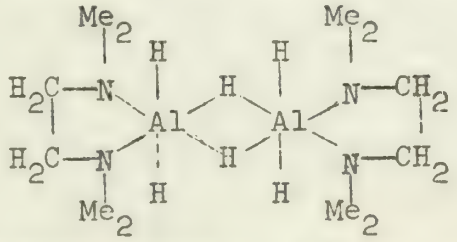
Association is believed to occur through hydrogen bridges or through dipole-dipole interaction in solution (13).

Tensiometric titrations by Ruff (21) confirmed an earlier report of penta coordinated aluminum in bis-trimethylamine alane (22). These studies also demonstrated the existence of bis- complexes for $Me_2NAllyl$ and Et_2NMe, but not for Et_3N and Pr_3N. The order of stabilities for bis-trialkylamine alane complexes is

$$Me_3N > Me_2NAllyl > Et_2NMe > Et_3N > Pr_3N.$$

Dipole moment studies (11) and single crystal X-ray analysis (23) both indicate that bis-trimethylamine alane is trigonal bipyramidal.

A novel adduct of alane and N,N,N',N'-tetramethylethylenediamine is reported to be a chelated dimer having the structure (24)



Dautel and Zeil (25) have reported an alane dioxane 1:1 adduct which behaves as a polymer. Apparently aluminum is penta-coordinate, and the dioxane is behaving as a bridging bifunctional ligand. Fetter and co-workers (26,27,28) recently have reported 1:1 trimethylalane adducts of trimethylhydrazine and tetramethyltetrazine. Proton resonance studies of the trimethylalane tetramethyltetrazine complex indicated that the tetramethyltetrazine was acting as a bidentate ligand.

Molecular complexes of alanes with other organo-metallic compounds are known. These are non-electrolytes and presumably electron deficient compounds. Among such complexes are $LiAlEt_4$, $EtMgAlEt_4$, and $Mg(AlEt_4)_2$ (29). Ruff (30) has recently prepared a 1:2 adduct of bis-dimethylamino alane and methylamino borane.

IV. ANIONIC COMPLEXES

Anionic complexes of the alanes are usually obtained by adding certain alkali metal compounds (MX), especially salts, to aluminum compounds of the general formula $AlR_{3-n}X_n$ (n=2 to 0). Typical compounds for addition are: alkali halides, pseudohalides, hydrides, alkyls, aryls, and alkoxyls. The stabilities of these anionic complexes follow certain rules. Large alkali metal ions and small halide ions produce the most stable metal halide alane complexes. The stability decreases with increasing size of the alkyl attached to aluminum: all trialkylalanes from methyl to butyl add NaF; $Al(C_6H_{13})_3$ does not (31). The stability of tetraethyl aluminate is demonstrated by the fact that the ethide ion displaces diethyl ether from the triethylalane diethyl ether adduct (32).

Bonitz (33) attributed the appreciable conductance of triethylalane to self-ionization of the type

$$Et_6Al_2 \rightleftharpoons Et_2Al^+ + AlEt_4^-$$

In addition to the type $MAlR_4$, there exists the 1:2 type complexes in which two molecules of the alane are added to the alkali metal compound (34). The 1:2 complex, $NaF:2AlEt_3$, is a liquid at room temperature and is a much better electrical conductor than $NaF:AlEt_3$ (35).

V. CONDENSATION REACTIONS AND ALUMINUM POLYMERS

Alane addition compounds of ammonia, primary amines, and secondary amines normally do not exist at room temperature due to an internal stabilization by splitting off RH. This condensation leaves an amino alane. The N-H and Al-R bonds are replaced by additional Al-N bonds to maintain tetra coordination for both aluminum and nitrogen (36). This leads to polymeric structures which are cyclic. If the amino alane has both N-H and Al-R bonds, it undergoes a second condensation step when the temperature is sufficiently high. This step produces insoluble, non-volatile, cross-linked, highly polymeric frameworks (37).

Wiberg and Gosele (38) reported that 1:1 and 1:2 alane pyridine adducts undergo an exothermic hydrogen migration at elevated temperatures. In the presence of excess pyridine, the product is tris-pyridino alane.

From the reaction of alane with excess ammonia, Wiberg has isolated, at different temperatures, $AlH_3:NH_3$, AlH_2NH_2, $AlH(NH_2)_2$, and $Al(NH_2)_3$ (39). Stepwise thermal decomposition of $AlH_3:NH_3$ gave AlH_2NH_2, $(AlHNH)_x$, and AlN (40). By means of the same procedure, the analogous derivatives of primary amines (41) and secondary amines (42) were prepared.

Ruff (43) has prepared bis- and tris-dialkylamino alanes by the reaction of trialkylamine alane adducts with dialkylamines. As discussed in section II, dialkylamino alanes are usually dimers or trimers. The compounds $(Me_2N)_3Al$ and $(Me_2N)_2AlH$ are associated in benzene, but $(i\text{-}Pr_2N)_3Al$ is monomeric. Longi and co-workers (44) have prepared $(Me_2N)_3Al$ and $[(C_6H_5)_2N]_3Al$ from the appropriate secondary amine and $(Me_2CHCH_2)_3Al$.

Nielsen and Sisler (45) reported the preparation of diethyl-2,2-dimethylhydrazino alane but did not isolate an adduct of triethylalane and N,N-dimethylhydrazine. Infrared data favor a six-membered ring structure. When heated,

the hydrazino alane condensed to a polymer having the composition $(MeH_2NNAlEt)_x$.

Laubengayer and co-workers (36) have allowed the adduct $MeH_2H:AlEt_2Cl$ to undergo successive condensation steps. The first condensation, at 50°C., yields (MeHNAlEtCl) and C_2H_6. The second step, at 210°C., yields $(MeNAlCl)_x$, which is a high polymer. The adducts $MeH_2N:AlEtCl_2$ and $Me_2HN:AlEt_2Cl$ undergo only one condensation step. These same workers have prepared the imino alane $(MeNAlC_6H_5)_x$, as the product of two successive condensation steps, from the adduct $MeH_2N:Al(C_6H_5)_3$. This imino alane and $(MeNAlCl)_x$ are both stable at 350°C. in a nitrogen atmosphere. However, both are hydrolytically unstable.

Fetter and his associates (26,27,28) have prepared polymers by the reactions of trimethylalane and substituted hydrazines and tetrazines. A polymer, having the composition $(MeAlNHNMe)_x$, prepared by the reaction of trimethylalane with methylhydrazine, decomposed at 200°C. Another polymer, $[Al(MeNNMe)_{1.5}]_x$, was prepared by the reaction of trimethylalane with 1, 2-dimethylhydrazine. Both of these polymers are hydrolytically unstable.

VI. CONCLUSIONS

Much of the recent published research dealing with alane chemistry is concerned with the alane amine adducts and their condensation products. Most of these investigations are designed to elucidate the character of the aluminum-nitrogen bond and the effects upon this bond of substitution on aluminum or nitrogen. The thermal stabilities of the aluminum-nitrogen polymers prepared thus far are quite encouraging. The major problem for future workers in this field is the preparation of a hydrolytically stable aluminum-nitrogen polymer.

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ROLL CALL

RATE OF A SUBSTITUTION REACTION IN CHLOROFORM
Ref: S. D. Ross and M. Finkelstein, J. Am. Chem. Soc. 79, 6547 (1957)

George Shier February 19, 1963

A detailed study of the rate of reaction of 2,4-dinitrochlorobenzene with n-butyl ammine showed that the rate constant was not constant for different initial concentrations of ammine. The reaction showed a positive neutral salt effect but no common ion effect with n-butylammonium salts. It was found that the reaction obeyed the rate law $K_2 = K_1 + K_7(nBaNH_2)$ where the K_1 term represents a path first order in both ammine and chloride and K_7 represents a path first order in chloride and second order in ammine. The mechanistic implications were discussed.

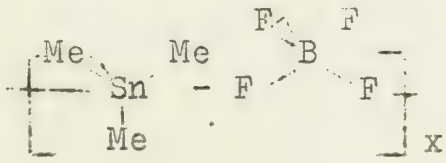
ROLL CALL

INFRARED STUDIES OF TRIMETHYLTIN COMPOUNDS

R. C. Burrows February 19, 1963

In an attempt to determine whether the free trimethyltin cation exists in the solid state, Okawara, Hathaway, and Webster(1) have examined the infrared spectra of the compounds $(CH_3)_3SnX$, where X represents ClO_4, NO_3 and $(CO_3)_{1/2}$. By comparing the number of bands predicted for various symmetry species and the number found for the trimethyltin and anion residues, they have shown that the cation $(CH_3)_3Sn^+$ is not present as such in these compounds, but rather that this group is covalently bound to the anion. The perchlorate is thought to have a polymeric structure involving five-coordinate tin, planar trimethyltin residues, and bidentate perchlorate groups. Although the nitrate and carbonate groups are probably also bidentate in their respective compounds, a non-planar trimethyltin residue was inferred here since both the symmetric and the antisymmetric C-Sn stretches are infrared active. Further structural details could not be derived for these two compounds on the basis of the infrared evidence alone.

An investigation(2) of trimethyltin tetrafluoroborate was also conducted by these workers along similar lines. The infrared spectrum of this compound corresponded to that which is theoretically predicted for a planar trimethyltin residue and a tetrafluoroborate group of C_{2v} symmetry. From these results the structure was assumed to be analogous to that deduced for trimethyltin perchlorate with the tetrafluoroborate group, generally considered to be a non-complexing anion, behaving as a bidentate ligand, as shown.



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ROLL CALL

BRIDGE ADDUCTS-THE INTERACTION OF BORON TRIFLUORIDE WITH TRANSITION-METAL CYANIDE COMPLEXES

Gerald Feistel February 19, 1963

A new class of compounds containing the M-C≡N-BF_3 linkage has been synthesized. The compounds, $K_2Ni(CN)_4 \cdot BF_3$, $K_2Ni(CN)_4 \cdot 4BF_3$, $K_4Mo(CN)_8 \cdot 7 \cdot 3\ BF_3$, and $K_4Fe(CN)_6 \cdot 3 \cdot 7\ BF_3$ have been formed by the reaction of BF_3 gas with the solid metal cyanide complexes at various temperatures and pressures.

A shift in the infrared band of the cyanide group and the appearance of new bands indicate the formation of the adduct. There is no change in the magnetism of the compounds of the Ni cyanides. Lack of simple metal cyanide-BF_3 ratios is attributed to a kinetic effect.

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N.M.R. COUPLING CONSTANTS AND HYBRIDIZATION IN ORGANO-TIN COMPOUNDS

J. C. Schapiro March 5, 1963

A relationship between ^{13}C-H nuclear magnetic resonance coupling constants and bonding hybrid orbitals has been shown to exist in a series of hydrocarbons (1, 2). The development of this relationship and its application to the bonding in some organo-tin compounds will be considered in the following sections.

THEORY

The Hamiltonian for a molecular system in a magnetic field may be expressed as the sum of four principal parts,

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_3 + \mathcal{H}_4$$

The term $\mathcal{H}_4$ is for the direct magnetic interaction of the nuclei with each other. This term may be neglected since it averages to zero in nuclear magnetic resonance experiments in which frequent collisions average the molecule over all orientations(3).

The term $\mathcal{H}_1$ includes terms for the kinetic energy of the electrons, their interaction as moving charged particles in the magnetic field of the nuclei, electrostatic potential energy, and the electron orbital-orbital, spin-orbital, and spin-spin interactions(4). $\mathcal{H}_2$ is the term for the dipole-dipole interactions between the nuclear magnetic moments and the electron magnetic moments. $\mathcal{H}_3$ is the contact term and is dependent upon the properties of electrons at the nucleus. The electron-coupled nuclear spin-spin interactions are those terms dependent on the spins of two interacting nuclei which arise when $\mathcal{H}_1$, $\mathcal{H}_2$, and $\mathcal{H}_3$ are discussed to the accuracy of second-order perturbation theory.

Ramsey(3) and Karplus(5) have shown that in cases in which the interacting nuclei are separated by one or two bonds, the largest and dominant contribution to the nuclear spin-spin interaction comes from the mechanism which corresponds to second order perturbations involving $\mathcal{H}_3$. These terms tend to be largest because they correspond to the electrons being close to the nuclei. The second-order perturbation energy for the operator $\mathcal{H}_3$ is

$$E_{2(1)MN'} = -\sum_{n(\neq 0)} \frac{(0|\mathcal{H}_3|n)(n|\mathcal{H}_3|0)}{E_n - E_0} \; ; \qquad \mathcal{H}_3 = \frac{16\pi\beta h}{3} \sum_k \sum_N \gamma_N \delta(\vec{r}_{kN}) \vec{S}_k \cdot \vec{I}_N$$

where: $E_n - E_0$ = the excitation energy between the singlet ground electronic state and the nth triplet excited state.

β = Bohr magneton = $e\hbar/2mc$

γ_N = magnetogyric ratio of nucleus N

$\vec{r}_{kN} = \vec{r}_k - \vec{r}_N$

$\delta\vec{r}_{kN}$ = Dirac function which picks out the value at $\vec{r}_{kN} = 0$ in any integration over the coordinates of electron k.

$\vec{S}_k$ = spin of electron k

$\vec{I}_N$ = spin of nucleus N

The coupling constant $J_{NN'}$ (in units of cycles per second) is defined by

$$= \langle I_{NN'} I_N I_{N'} \rangle$$

where $E_{NN'}$ is the energy of interaction between two nuclei with spins of I_N and $I_{N'}$ (units of $\hbar$) (6). If one uses the energy of interaction contributed by the $\mathcal{H}_3$ term only, then the above equation defines $J^{(3)}_{NN'}$, the coupling constant which arises from the contact term alone. It can be shown that

$$J^{(3)}_{NN'} = -\frac{2}{3\hbar}\left(\frac{4\pi\beta\hbar}{3}\right)^2 \gamma_N \gamma_{N'} \frac{1}{\Delta E} \times \left[0 \left| \sum_k \sum_j \delta(\vec{r}_{kN})\, \delta(\vec{r}_{jN'})\, \vec{S}_k \cdot \vec{S}_j \right| 0\right]$$

In deriving the above equation the singlet-triplet excitation energies are approximated by a mean value ΔE. The limits of this approximation have been discussed by Ripka (7). Evaluation of $J_{NN'}$ then depends upon the wave function, 0, for the ground electronic state.

Using a generalized valence-bond function

$$0(1,2) = \eta(\lambda_N \lambda_{N'}) \{ \phi_N(1)\phi_{N'}(2) + \phi_N(2)\phi_{N'}(1) + \lambda_N \phi_N(1)\phi_N(2) + \lambda_{N'} \phi_{N'}(1)\phi_{N'}(2) \}$$

where ϕ_N and $\phi_{N'}$ are hybrid orbitals on nuclei N and N' respectively, λ_N $\lambda_{N'}$ are parameters determining the charge distribution and $\eta(\lambda_N, \lambda_{N'})$ is the appropriate normalizing factor with inclusion of overlap, $J^{(3)}_{NN'}$ becomes a function of the degree of hybridization in the atomic orbitals ϕ_N, $\phi_{N'}$, and the bond polarizations λ_N, $\lambda_{N'}$ (1). The term $J^{(3)}_{NN'}$ is dependent upon the amount of s character in the hybrid atomic orbital, since the s orbital does not have a nodal plane at the nucleus.

Two additional points need to be considered in choosing the wave function for $J^{(3)}_{NN'}$. First if the two interacting nuclei are directly bonded to each other, only the perfect pairing structure contribution to the ground-state wave function need be taken into account; if the two nuclei are not joined through a single sigma bond, the non-perfect pairing structures contribute to make $J^{(3)}_{NN'}$ non-zero. Secondly, Muller and Pritchard(2) and Juan and Gutowsky (8) have shown that J_{CH} in the C^{13}-H group is relatively insensitive to the value of λ_{C-H} (ionic character of the bonds) within certain limits. However, J_{Si-H} for the ^{28}Si-H group has been shown to be dependent upon λ_{Si-H} due to the greater polarizability of Si as compared to C(8). It might be expected then that ionic contribution to the wave function would be important in the case of the other group IVB elements.

APPLICATION OF THE THEORY

For any group IVB element, M, the Fermi contact contribution to the coupling constant J_{M-H}, using a valence bond wave function for the perfect pairing structure, may be expressed as

$$J_{M-H} = \frac{\gamma_M \gamma_H}{\hbar \Delta E}\left(\frac{4\pi\beta\hbar}{3}\right)^2 \eta^2 \alpha^2 |\psi_{s_M}(0)|^2 |\psi_{s_H}(0)|^2$$

where α^2 is the s character of the M hybrid for the M-H bond.(8) n_s (0) is the n_s wave function evaluated at the M nucleus. If non-perfect pairing structures are to be considered, the expression becomes more complicated but it is still linearly dependent on the amount of s character in the hybrid orbital on M. Therefore, one may to a first approximation determine changes in hybridization in a given series of compounds by observing trends in the coupling constants for those compounds.

METHYLTIN HALIDES

Natural abundance tin contains three nuclides with spin of 1/2, ^{115}Sn, ^{117}Sn, and ^{119}Sn. The abundances are ^{115}Sn, $<1\%$, ^{117}Sn, 7.67%, and ^{119}Sn, 8.67%. Spin-spin couplings due to ^{115}Sn are not observed experimentally. Holmes and Kaesz(9) and Van der Kelen (10) have studied the tin-hydrogen splitting on the proton resonance in a series of methyl tin halides. Holmes and Kaesz indicate that the contact mechanism makes the dominant contribution to Sn-C-H coupling and that except for rehybridization of the tin atom, other components of the bonding system Sn-C-H do not change appreciably. They point out that the assumption receives some support from the fact that the ^{13}C-H spin-spin interactions vary by a very small amount in this series of compounds. As a Cl atom is substituted for a CH_3 group the coupling constant $J_{\underline{Sn}-C-\underline{H}}$ increases indicating a larger amount of s character in $\underline{Sn}-C-\underline{H}$ the tin bonding orbital towards carbon; this following Bent's argument for "second order hybridization" effects (11, 12).

In H_2O and D_2O solutions the formation of ions such as Me_3Sn^+, Me_2Sn^{2+} and $MeSn^{3+}$ indicates entirely different hybridization states for the tin atom. Abrupt changes in $J_{\underline{Sn}-C-\underline{H}}$ are observed similar to those observed for $J_{\underline{C}-\underline{H}}$ in carbon compounds where hybridization changes from sp^3-sp^2 to sp (10). Burke and Lauterbur(13), observing proton coupling on the ^{119}Sn resonance, found $J_{\underline{Sn}-C-\underline{H}}$ for $(CH_3)_2SnCl_2$ to be 80 c.p.s. in acetone and 98 c.p.s. in H_2O, which they attribute to the existence of alkyl-tin-chloride-solvent complexes. Although the $(CH_3)_3SnBr\cdot py$ complex is very stable, the observed change in $J_{\underline{Sn}-C-\underline{H}}$ is rather small; Van der Kelen attributes the small change in J to a small change in the hybridizational state of tin(10). In light of the recent work by Matwiyoff (14), who has found that the Sn-H coupling constants in $(CH_3)_3SnCl$ increase about 10 c.p.s. when measured in TMSO, it appears that the small change in $J_{\underline{Sn}-C\underline{H}_3}$ found for the pyridine complex in $CDCl_3$ solution may be attributed to the diluteness of the solution and perhaps dissociation of the $(CH_3)_3SnBr\cdot py$ complex.

OTHER ORGANO-TIN SYSTEMS

Recently, Flitcroft and Kaesz (15) have observed in the SnH_4, methylstannane series, trends similar to those in the methyltin halide series that are similarly explained by a combination of the theory of spin-spin coupling and the effects of the electronegativity of a substituent on the hybridization

TABLE 1 - COUPLING CONSTANTS IN METHYLTIN HALIDES (in c.p.s.)

COMPOUND	SOLVENT	$J_{C^{13}-H}$	$J^{117}_{Sn-CH_3}$	$J^{119}_{Sn-CH_3}$	REF.
$(CH_3)_4Sn$	neat	-	51.5	54.0	9
	CCl_4	-	51.4	53.8	9
	$CDCl_3$	128.4	52	54.3	10
$(CH_3)_3SnCl$	neat	-	57.4	59.7	9
	CCl_4		56.0	58.9	9
	$CDCl_3$	133	56.4	58.6	10
	H_2O	-	65.2	68.4	9
	D_2O	134	67.7	70.7	10
$(CH_3)_2SnCl_2$	neat	-	68.0	71.0	9
	CCl_4	-	66.6	69.7	9
	$CDCl_3$	137.8	67	69.5	10
	H_2O	-	97.4	101.9	9
	D_2O	134	102.5	107.5	10
CH_3SnCl_3	neat	-	95.7	100	9
	CCl_4	-	95.3	99.5	9
	$CDCl_3$	-	93.4	98.5	10
	H_2O	-	125.4	131.1	9
$(CH_3)_3SnBr$	$CDCl_3$	134	56	58.6	10
$(CH_3)_3SnBr \cdot py$	*$CDCl_3$	134	59.8	62.1	10
$(CH_3)_3SnCl$	**TMSO		68.0	70.0	14

*Probably a dilute solution
**TMSO = tetramethylene sulfoxide

of a central atom. However, the effect of substituting CH_3 for H on the coupling Sn-H in this series is not strictly additive. As indicated in the first section of this abstract, Juan and Gutowsky(8) have attempted to explain deviations in the silanes and one might expect similar effects in the stannanes.

Brown and Morgan (16,17) have observed that increasing catenation in polystannanes results in a decrease in J_{Sn-CH_3} and a slight increase in $J_{Sn-Sn-CH_3}$, indicating more s character in the tin-tin bonds as the number of tin-tin bonds increases in a given molecule. Further support for this is given by the fact that the tin-carbon stretching frequencies were found to increase linearly with the coupling constant for the series studied.

Drago and Matwiyoff (14,18) have studied the $J_{C^{13}-H}$ values for a series of tetramethyl derivatives of group IVB elements and find the coupling constant values parallel the M-C bond energies.

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MOLECULAR EXCITATION IN SHOCK TUBES

Sue F. Eilers March 21, 1963

I. INTRODUCTION

Investigators concerned with the effects of shock waves produced by supersonic aircraft and in nuclear explosions discovered that the shock tube could be used to study the pressures due to shock waves and that these waves produce high temperatures in the gases through which they pass (1,2). It is this property which has made them of interest to chemists.

II. THEORY (1-22)

At the instant the diaphragm in the shock tube is ruptured, the molecules of gas in the low-pressure section of the tube are moving over relatively long mean free paths, as a consequence of the low density of the gas, and at an average speed of about 1,000 feet per second. Compression of the gas in the first little slab ahead of the outrushing piston of high-pressure gas shortens the mean free path of the molecules and steps up their rate of collision, thereby increasing the mean velocity and, consequently, the temperature of the gas. The first minute disturbance passes forward at the speed of sound into the next slab, compressing and preheating it for the arrival of the next wave, thus causing that wave to move faster. As the waves overtake one another building up into a large pressure pulse and as the pressure pulse grows into a shock wave, the mean free path of the molecules in the wave grows still shorter, and the temperature rises.

The shock wave must spread out over some finite distance in the gas, measureable in terms of the length of the mean free path. Across this distance the gas density, temperature, pressure, and velocity all change. As the shock wave forms and these gradients grow steeper, energy in the form of heat and momentum flows more swiftly from regions of high temperature and velocity to regions of low temperature and velocity in the wake of the wave (1, 23-35). Ultimately, the opposing mechanisms of steepening and spreading balance and the shock wave profile becomes stable.

At this point, other phenomena may be observed. By no means is all of the kinetic energy of the shock wave transformed into heat in the form of translational energy. In fact, with each increase in temperature an increasing percentage of the energy is transformed into other energy modes.

In the zone of highest temperature just behind the shock front, the molecule-molecule collisions cause rotation as well as elastic collisions. Back a little farther, the interatomic bonds begin to vibrate. The transformation of energy from translation to rotation to vibration is known as energy relaxation, and it has been demonstrated by numerous experiments in diatomic and polyatomic gases (79-92). As the translational energy (and along with it the temperature) drops from its highest value immediately behind the shock wave

front to a lower value some distance behind it, the gas density behind the shock front changes accordingly. These density profiles show up in photographs made with the Mach-Zender interferometer and can be used in calculating the time required to transform energy from one mode to another. These relaxation times are an indication of the number of molecule-molecule collisions necessary to produce the energy transfer. The collision cross section for energy exchange between two molecules can thereby be computed and compared with values calculated from quantum theory. Other methods for studying these phenomena include x-ray, infrared and ultraviolet spectroscopy (36-45). Both experiment and theory show that for all but the weakest shock waves, the translational and rotational energies are quickly activated, usually within a few mean free paths, whereas the vibrational mode lags considerably in activation, as a result of the small probability of vibrational transitions. Experiments detecting this can be interpreted in terms of a vibrational relaxation time or a vibrational transition probability (6,9,13,19,79-92). It is difficult to deduce from these experiments the mechanics of the collision in which a given vibrational transition takes place, since what is measured is the transition probability averaged over a Maxwellian distribution of translational energies. However, considerable progress is being made in the theory of these low-energy collisions, and proper predictions of vibrational relaxation times are one test of their validity. Also, molecular beam experiments are valuable supplements to shock tube measurements in this regard.

It was not long after the invention of the shock tube that investigators noticed that the hot gases in the tube emit light. In fact, when a gas has attained a sufficiently high temperature, this is one of the principal modes by which energy is dissipated. This process involves electronic transitions from one quantum state to another. For any given temperature, there is a specific distribution of electron-energy states throughout the atoms in the gas. The electrons deexcite either by quantum jumps or as the result of inelastic collisions. The higher the temperature, the greater the number of inelastic collisions causing excitation and, consequently, the greater the number of photons emitted.

The mean lifetime of the excited state is in principle calculable from theory; however, such calculations are prohibitively difficult for all but the simplest atoms and molecules. While experimental results obtained by heating gases with arc and spark discharges are blurred by the introduction of impurities from the electrodes, the shock tube provides impurity-free hot gases at temperatures and densities that can be precisely controlled by adjustment of the pressures in the two sections of the tube (1,9,10,73-78).

Other studies done in shock tubes include kinetics (46-54), high-temperature reactions (55-61) and measurement of dissociation constants (62-72).

III. A SPECIFIC CASE: STUDIES OF VIBRATION RELAXATION IN NITROGEN (II) OXIDE

Since one of the most interesting of the experiments done in shock tubes is the determination of vibrational relaxation times, and there have been several papers on nitrogen (II) oxide, giving parameters at a wide temperature range, this was chosen as an example of the type of data which can be obtained.

In the earliest of these studies (89), nitrogen (II) oxide was examined at temperatures less than 1000°K. It was assumed that no dissociation took place in these experiments and that the ideal gas law was valid. Because of the small excitation of the vibrational levels, only the first vibrational level was considered in the relaxation time. The formula for the transition probability was found to be

$$P_{10} = 2.86/\tau_1 P_1 (\sigma/\rho)^2 (T_a)^{1/2} \qquad (1)$$

where P_{10} is in mm. of mercury, τ_1 in microseconds, T_a in degrees K. Using Lennard-Jones parameters ($r_0 = 3.6 \times 10^{-8}$ cm., $\epsilon/k = 91°K$), it was found that the experimental measurements for relaxation were about 5×10^5 as large as the calculated values. However, fitting the Lennard-Jones potential formula to data including the possibility of dimer formation, Robbens found $\epsilon/k = 2000°K$ and $r_0 = 2.15 \times 10^{-8}$cm. When P_{10} was calculated using these parameters, the values agreed fairly well.

Robbens had used ultraviolet light to examine the vibrational mode inthis oxide. Later his data was compared with the infrared data of Monson and Allport (from the same laboratory), with very good correlation (92).

Roth examined nitrogen (II) oxide at temperatures between 5000 and 10,000°K (Tables I and II) a range where the gas was considered to be excited (90).

Wrey has examined nitrogen (II) oxide at temperatures between those above and those of Robbens. Using the following equations, he found the probabilities of transitions.

$$P_{10} = A_3(\bar{\epsilon} - \epsilon_0)^{-1/2}, \quad T > \epsilon_0/k \qquad (2)$$

$$P_{10} = A_4 T^{-1} \exp(-\epsilon_0/kT), \quad T < \epsilon_0/k, \qquad (3)$$

where A's = constants determined experimentally and $\bar{\epsilon}$ = average kinetic energy of colliding molecules at infinity. Using the second set of parameters from Robbens, he found the predicted values to be higher than the experimental by a factor of about 20. Extrapolation to lower temperatures of Wrey's values for P_{10} gives much lower values than those calculated by Robbens. However, Wrey apparently also assumed absence of excited states, which, as the temperature rises, is an increasingly poor assumption.

IV. CONCLUSION

The shock tube provides a relatively easy, very fast method for heating gases to high temperatures. At intermediate temperatures, it may be used for the study of vibrational modes in excited states, as in the studies discussed here. At slightly higher temperatures, it may be used to study dissociation rates and constants. At still higher temperatures, such as those produced by electromotive shocks, the phenomena of plasmas become available for study (21,22). Therefore, it seems apparent that shock tubes will become increasingly familiar laboratory apparatus and that they should provide some interesting answers to many questions concerning fundamental physical problems.

TABLE I (90)

Relaxation times for V = 1 → V = 0 in ($A^2\Sigma^+$) state of NO

T, °K	ρ Xe (a) 10^{17} cm^{-3}	Mole % Air	τ, μsec
9900	1.25	2.5	34
8875	1.30	5.0	32
8875	1.30	5.0	49
8825	1.24	2.5	31
8275	1.24	2.5	39
7975	1.29	5.0	49
7400	1.29	5.0	91
7125	2.47	2.5	56
6950	2.47	2.5	41
6700	2.46	2.5	46
6650	2.56	5.0	64
6375	2.55	5.0	56
5425	2.54	5.0	106

a) Initial pressures in the low pressure section of the shock tube were 1 mm. and 2 mm. for ρ Xe = about 1.25×10^{17} cm^{-3} and about 2.5×10^{17} cm^{-3}, respectively, where ρ refers to the density of the element in molecules/cm^3.

TABLE II (90)

Relaxation times referred to density at 1 atm. pressure for $V = 1 \rightarrow V = 0$ in NO ($A\ ^2\Gamma^+$).

T, °K	5000	6000	7000	8000	9000	10000
τ, sec.	28	18	12	8	6	5

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BORON POLYMERS

Gerald Tennenhouse March 26, 1963

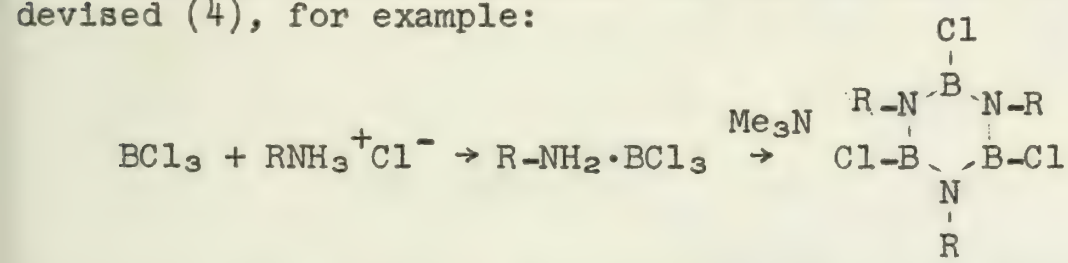
Boron compounds are of particular interest in the mushrooming field of inorganic polymers. This is due in part to the chemical and thermal stability of certain boron-nitrogen, boron-phosphorus, and boron-oxygen compounds. However, their popularity is also due to the exhibition of properties usually associated with organic polymers (18, 19).

It is convenient to divide the topic of boron-containing polymers into four loosely organized groups: compounds characterized by boron-nitrogen bonds; compounds characterized by boron-phosphorus bonds; compounds characterized by boron-oxygen bonds; and compounds which do not readily fit into any of the above-mentioned categories.

BORON-NITROGEN POLYMERS

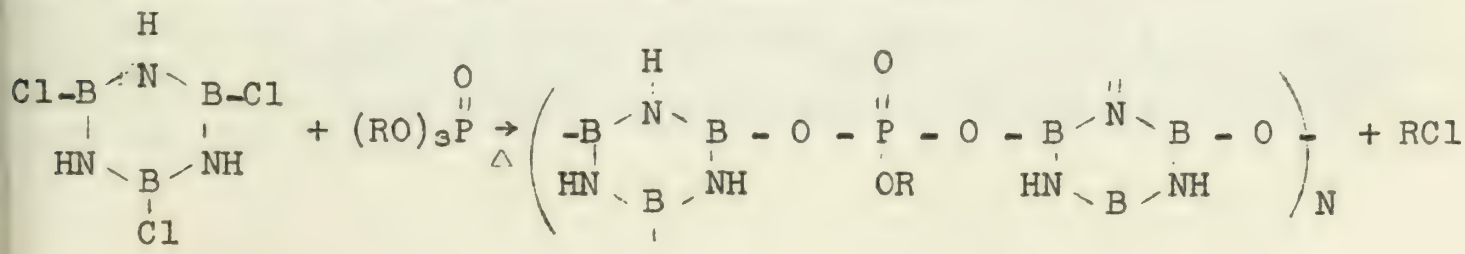
Borazole was first prepared by Stock and Pohland (1) by the reaction of ammonia and diborane. The heat stability of borazole itself and various substituted borazoles (2, 3) has prompted investigations of boron-nitrogen chemistry in the hope of discovering heat-stable inorganic polymers.

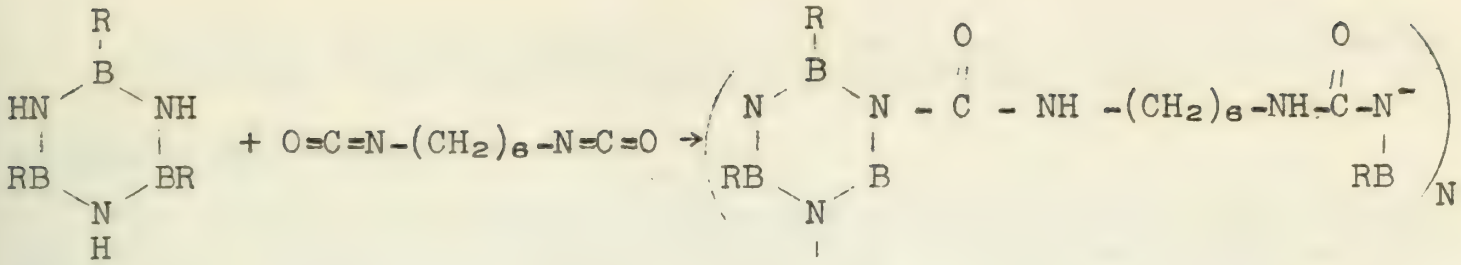
Several improved methods for the synthesis of borazoles have been devised (4), for example:



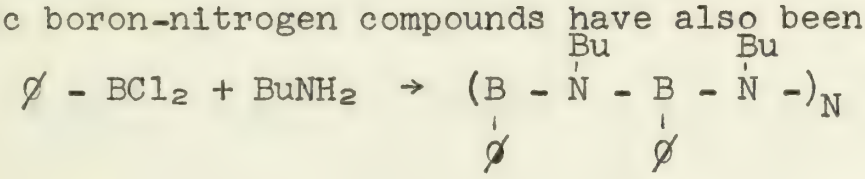
The B-Cl chlorine atoms may then be replaced by alkyl or aryl groups by the action of Grignard reagents. Other anions, such as CN^-, CNS^-, NO_2^-, and RO^- may be introduced by the action of an appropriate metal salt on an ethereal solution of the B-Cl borazole (4).

A great many attempts have been made to prepare high molecular weight inorganic polymers by joining borazole rings in one manner or another. The ultimate result of such work is hexagonal boron nitride. However, the degree of cross linking is so high that the material does not have the flexibility usually associated with the term polymer and is of little commercial use. Some attempts to join borazole rings are illustrated by the following examples (7):

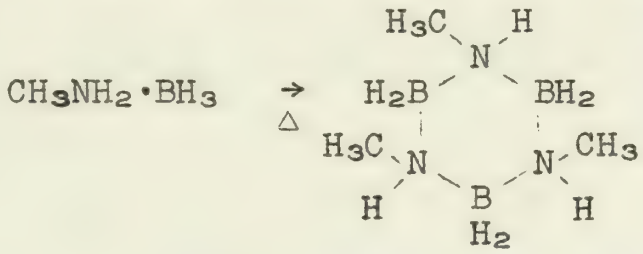


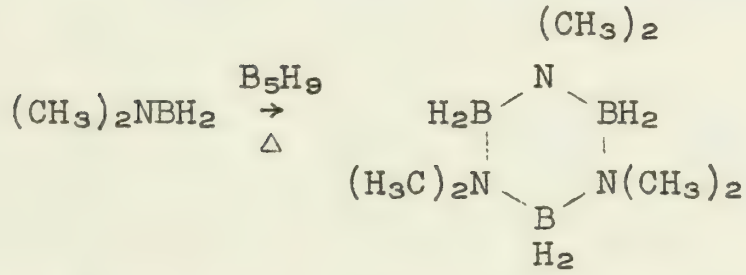


Non-cyclic boron-nitrogen compounds have also been prepared (2):



Borazole is commonly referred to as inorganic benzene. However, another series of boron-nitrogen compounds has been prepared which may be thought of as saturated (11, 12), for example:





Both of these compounds show unusual resistance towards hydrolysis as well as good thermal stability.

BORON-PHOSPHORUS POLYMERS

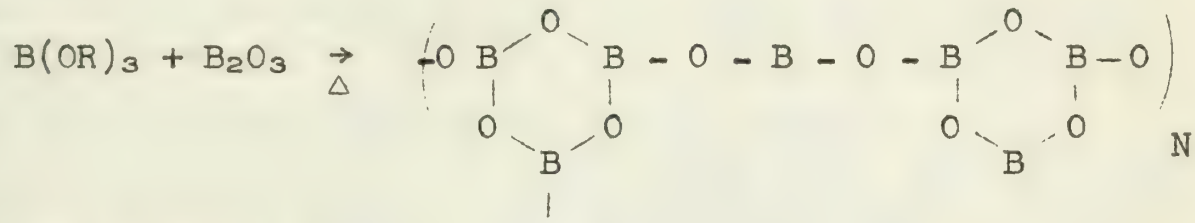
Boron-phosphorus chemistry is a relatively new field. Gamble and Gilmont (10) first caused phosphine and diborane to react and obtained a poorly characterized white solid which was thought to be a highly cross-linked polymer.

Burg (9) found that more distinct compounds could be obtained by the use of dimethyl phosphine instead of phosphine. The compounds obtained by Burg were found to have remarkable chemical, as well as thermal, stability.

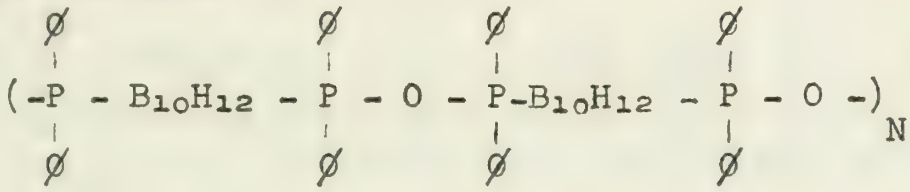
Both Burg (13) and Wagner (14, 15) have developed improved methods of synthesizing both boron-phosphorus monomers and polymers.

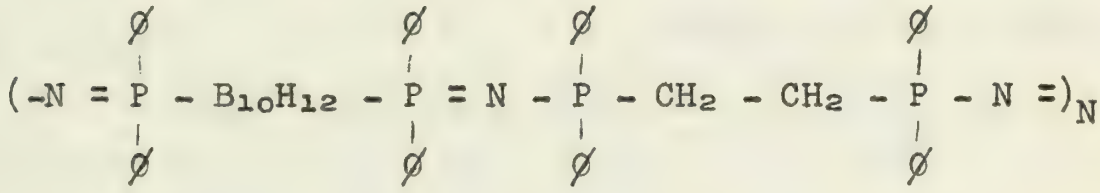
BORON-OXYGEN POLYMERS

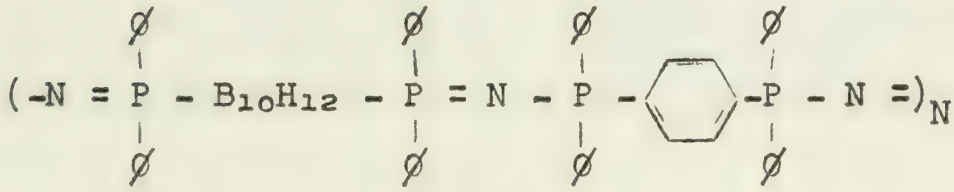
The boron-oxygen system of polymers is very attractive because of the low cost and relative ease of handling of the starting materials. Unfortunately, many of these compounds are easily hydrolyzed. A typical synthesis may be formulated as (2):



MISCELLANEOUS POLYMERS







Some of these compounds show good thermal and chemical stability, as well as exhibiting certain properties usually associated with organic polymers.

A great many compounds have been prepared which do not fit conveniently into any broad category. Examples include the polymer obtained from the reaction of diborane and hydrogen sulfide (21); the product of the reaction between B_5H_9 and acetylene in a discharge tube (2); and the product of the reaction between diborane and carbon monoxide in a discharge tube (2). These and other reactions have yielded products that have been identified as polymers. However, these polymers do not seem to be of interest at the present time.

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MACROCYCLIC COORDINATION COMPOUNDS

E. J. Olszewski March 28, 1963

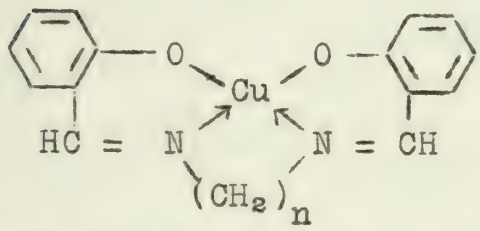
Introduction

While metal-chelate compounds having five- and six-membered rings are well established in the literature, evidence for rings of larger size is not as conclusive. O'Brien (1) showed that, while many macrocyclic metal complexes had been reported, the great majority of structures had been postulated on the basis of analytical data alone. Lack of x-ray data, the possibility of several linkages, or of polymerization served to make the existence of large rings doubtful. However, the utilization of rigid geometrical structures and increasing use of physical measurements, have made possible the isolation and characterization of macrocylic rings. These are essentially of three types; inner complexes, compounds with the $Cu_2(C_2H_3O_2)_4 \cdot 2H_2O$ structure, and ferrocene derivatives.

Rigid Templates

The formation of normal five- or six-membered chelates often serves as a frame to which larger rings may be attached.

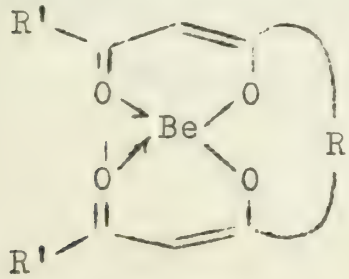
Magnetic susceptibility measurements (2) on



n = 5, 6, 7

showed the paramagnetism of the copper(II) ion to decrease as n increased. The stability of the salicylaldimine ring and the flexibility of the hydrocarbon chain could account for the formation of these complexes.

Monomeric and dimeric species of beryllium (II) tetraketones have been reported on the basis of analytical data, molecular weight determinations, and infrared spectra (3).



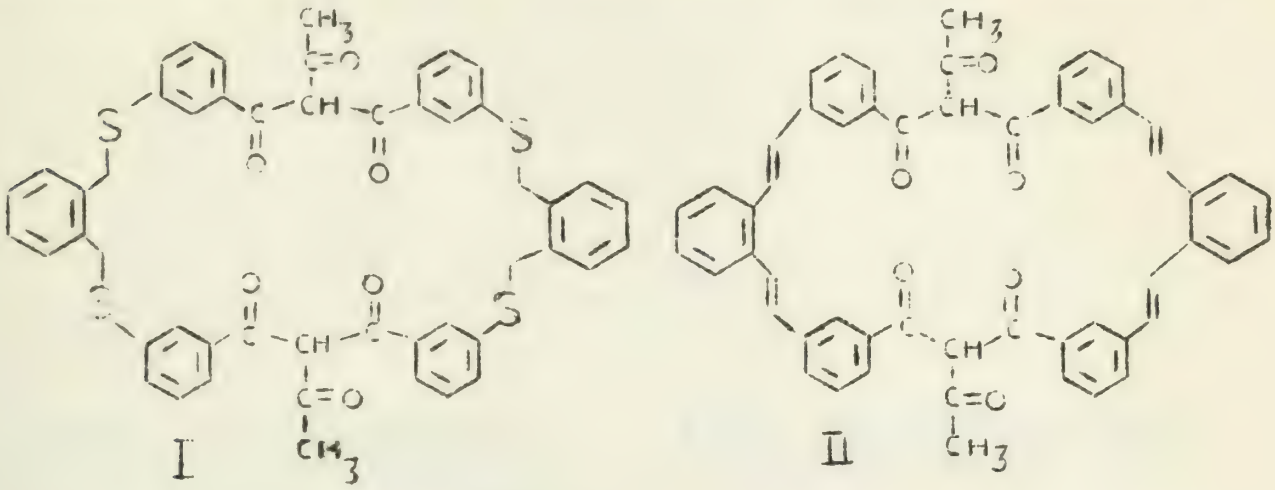
$R = -(CH_2)_n-$ where n = 6, 7, 8, 10, 12

$R = -NH(CH_2)_mNH-$ where m = 6, 10

$R = -O(CH_2)_pO-$, where p = 6, 10

When R is small, e.g. $-(CH_2)_6-$ or $-O(CH_2)_4O-$, then dimerization is favored. In both cases, however, the compounds are prepared by thermal degredation of the corresponding low molecular weight polymers.

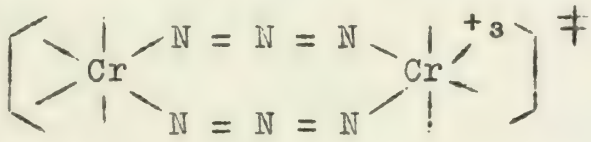
Divalent copper and magnesium macrocycles of bis-(1,3-diketones) have been isolated by Coombs and Houghton (4). Their observations are supported by analyses, molecular weight data, and infrared spectra. They report the copper(II) chelates of



and divalent copper and magnesium chelates of similar species. The chelates are utilized in the preparation and isolation of smaller ligands.

Azide Dimers

Snellgrove and King(5) postulated an eight-membered ring

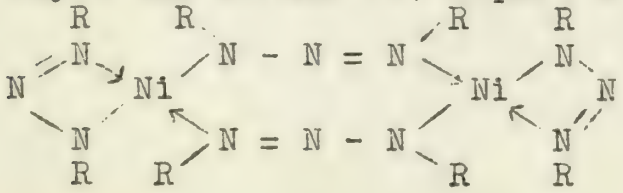


intermediate in the exchange between chromium(II) ion and cis-diazidotetraaquochromium(III) ion:

$$Cr(N_3)_2^+ + {}^*Cr^{+2} \rightleftharpoons Cr^{+2} + {}^*Cr(N_3)_2^+$$

For a transition state with a single azide bridging group, net aquation would have resulted in giving monazidochromium(III) ion and hydrazoic acid. Also exchange of monazidochromium(III) ion and chromium(II) ion under the same conditions gave k = 1.3 l/mole/sec as opposed to 60 l/mole/sec.

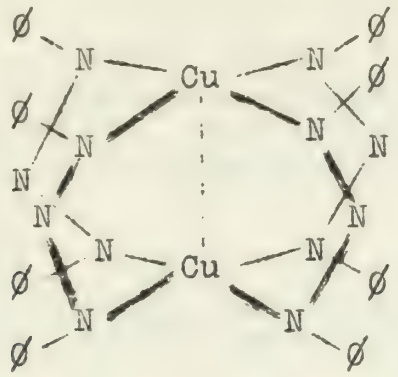
Dwyer and Mellor (6) report a dimeric structure for



R = C_6H_6 or p-$C_6H_4 \cdot CH_3$

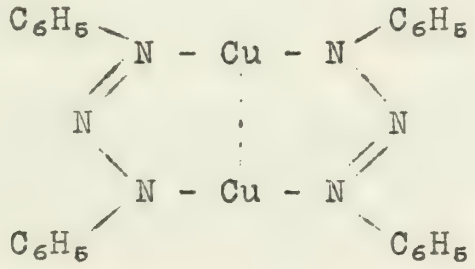
The compounds are diamagnetic, and dimeric in benzene. The solid forms red crystals. In boiling benzene the molecular weight shows a breakdown, but on cooling the dimer is re-formed.

The analogous copper(II) complex of 1,3-diphenyltriazen was studied by Harris and Martin (7) and found to be diamagnetic in the solid state and in benzene. They postulated the following structure:



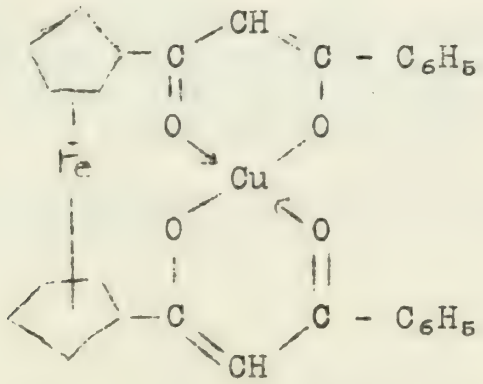
Harris, Hoskins and Martin (8) found the divalent nickel, copper and palladium complexes of 1,3-diphenyltriazen to be dimeric in benzene and diamagnetic.

Crystal studies by Brown and Dunitz (9) on the copper(I) chelate of diazoaminobenzene show a planar structure with a linearly coordinated copper atom. The N-Cu-N angle is almost linear.



Ferrocenylene Frames

Hauser and Cain (10) reported a macrocycle with two different metal ions. The compound was a -diketone salt of divalent copper derived from the corresponding ferrocene derivative:

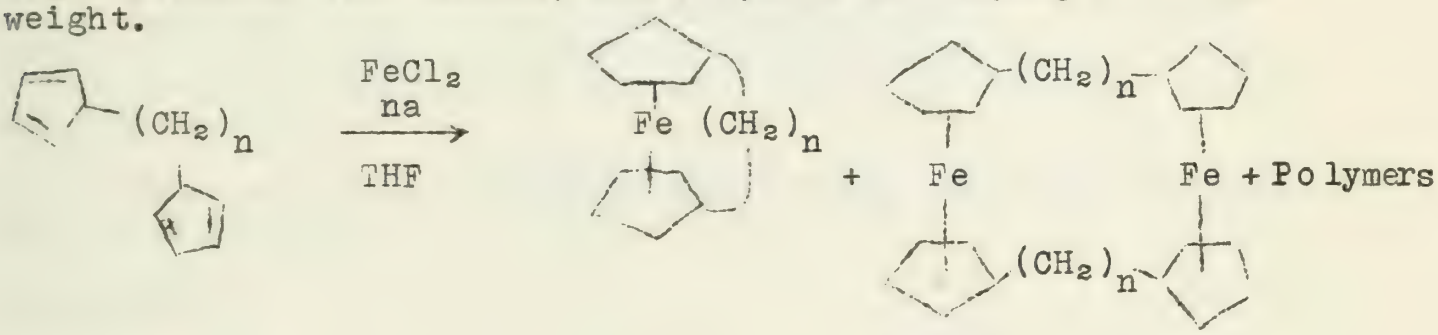


The yellow powder was recrystallized from benzene and melted above 300°C.

Heterocycles containing silicon bridges were isolated by Schaaf and co-workers (11) from 1,1'-bis-(dimethylethoxysilyl)-ferrocene. Structural assignments were made on the basis of infrared spectra and molecular weight determinations.

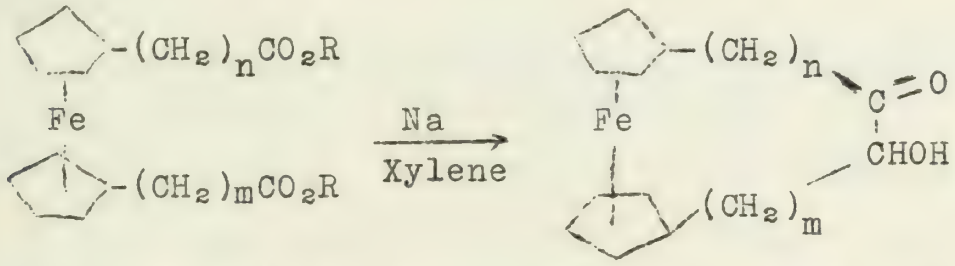
Rinehart and Curby(12) showed that cyclization would be heteroannular or homoannular depending on the size of the chain in the starting material. The product formed by homoannular ring closure could be distinguished by the absence of IR bands at 1110 and 1004 cm^{-1}.

Lüttringhaus and Kullick (13) obtained bridged ferrocenes in low yields from α,ω-bis-(cyclopentadienyl)-alkanes. The major products were dimers, and polymers of varying molecular weight.



n	3	4	5
% yield	2.5	0.053	0.025

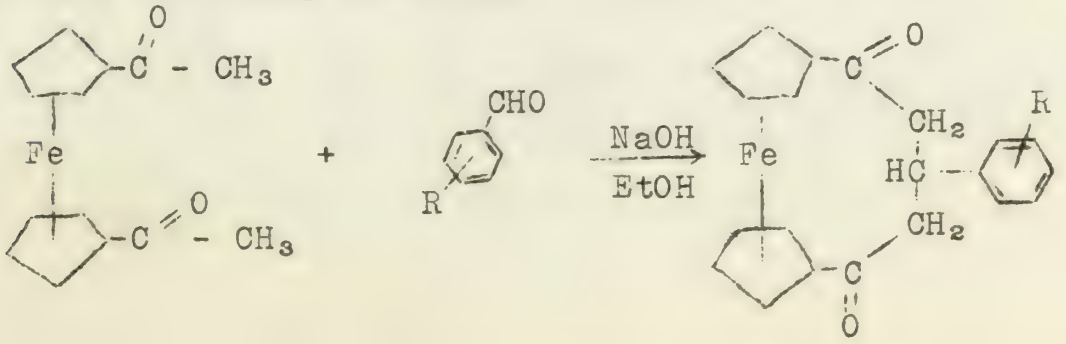
Treatment of ferrocene-1,1'-bis-(propionic acid) with trifluoroacetic anhydride (14) gave 1,1':3,3'-bis-(trimethylene)-ferrocene, after reduction. Schlögl and Seiler (15) also isolated a series of acyloins in various yields:



n	m	% Yield
1	1	20
2	2	50
3	3	40-58
3	4	55
4	4	75

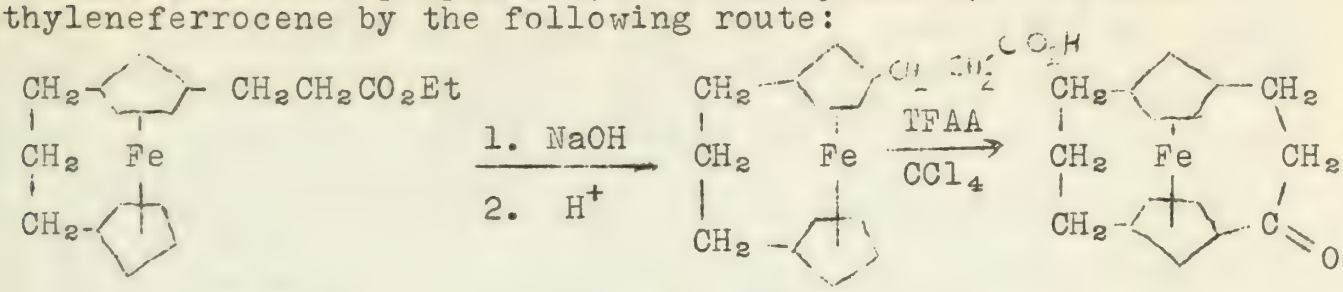
Hauser, Cain and Mashburn (16) treated diacetyl ferrocene with benzaldehyde and aqueous NaOH to get a small amount of cyclic product. While they postulated a monomeric structure, the possibility of a dimer was not ruled out.

Furkik and co-workers (17) obtained yields from 10-78% for the following reaction:



R = H, o-Cl, m-NO_2, 3,4-OCH_2O-

Gustafson (18) prepared 3,3'-trimethylene-1,1'-α-ketotrimethyleneferrocene by the following route:



Brown (19) was able to reduce the product by means of H_2 and platinum.

Other reducing agents were examined by Gustafson (18), who found that reduction was quantitative when a 10/15 mole ratio of $LiAlH_4/AlCl_3$ was used as opposed to a 63% yield when $LiAlH_4$ was used alone. The products were characterized by IR and NMR spectra.

Other compounds containing large rings were also isolated by Gustafson (18).

Conclusion

The preparation of macrocyclic chelate complexes is possible if coordinating ligands can be attached to a rigid molecular frame. At present the ferrocenylene structure seems to be the most promising as evidenced by the variety of ferrocene complexes already reported in the literature. Unfortunately very little work on crystal structure has been done on these compounds.

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E. S. R. OF TRANSITION METAL ION COMPLEXES

Peter C. Van Der Voorn April 2, 1963

In electron spin resonance we study the absorption of electromagnetic radiation which effects transitions between energy levels of the spin states of unpaired electrons. By application of an external magnetic field it is possible to vary these energy levels. Since the energy differences are of the order found in the microwave region, absorption of microwave radiation is studied. In some aspects ESR is similar to NMR where the transitions studied occur between energy levels of the nuclear spin states, again after the application of an external magnetic field.

The instrumentation consists of a monochromatic source of microwave radiation, an absorption cell in a magnetic field at right angles to the beam of radiation, and a detector. Measurements are most commonly made at 1.25-3 cm wavelengths with fields ranging from 8000-3000 gauss. Although in principle either the microwave frequency or the field strength can be varied while the other is held constant, in practice it is simpler to vary the field strength.

The spin angular momentum M_S (spin S) of an electron can have values of $\pm 1/2$. In the absence of a magnetic field, there is no preference and the spin energy is doubly degenerate. After a magnetic field is applied the electron precesses about an axis parallel to the field. By absorbing a quantity of radiation $h\nu$, the spin changes and the electron precesses about an axis anti-parallel to the field. The resonance condition is given by $h\nu = g\beta H$, where h is Planck's constant, ν the frequency of radiation, β the Bohr magneton, H the strength of the magnetic field and g, a proportionality constant which has the value of 2.0023 for a free electron. In general with n unpaired electrons, the spin degeneracy is n+1 and is split by the magnetic field into n+1 levels; n transitions can then occur between the $_S$ levels under the selection rule $M_S = \pm 1$.

When one considers the unpaired electrons in transition metal ions in the solid state, it is necessary to take into account the complete energy state of the ion. The complete Hamiltonian can be written as (6):

$$W = W_F + V + W_{LS} + W_{SS} + H(L + 2S) \cdot W_N - \gamma\beta_N H.I.$$

where W_F includes the energies of the free ion in the gaseous state ($\sim 10^5$ cm^{-1}); V is the electrostatic energy due to the crystal field (10^3-10^4 cm^{-1}); W_{LS} represents the spin-orbit coupling ($\sim 10^{-2}$ cm^{-1}); W_{SS} the magnetic interaction between electrons (~ 1 cm^{-1}); $H(L + 2S)$ the effect of the external magnetic field (1 cm^{-1}); W_N interactions due to the nucleus ($\sim 10^{-2}$ cm^{-1}) and $\gamma\beta_N HI$ the effect of the magnetic field on the nuclear magnetic moment (10^{-3} cm^{-1}); this latter effect can usually be neglected in ESR.

When a gaseous ion is placed into a crystal, the degeneracy of the d-orbitals will be resolved by the crystal field: for example, for Cu^{2+} the ^2D ground state of the free ion becomes orbitally non-degenerate after considering the effects of a cubic field and a tetragonal distortion, but the spin degeneracy is not affected. In some metal ion crystals the spin degeneracy can also be resolved by the crystal field, but only through spin orbit coupling. This is called zero-field splitting (e.g. Cr^{+3}). However in the case of an odd number of unpaired electrons the spin remains doubly degenerate; this is known as Kramer's degeneracy (23). In any case the spin degeneracy is completely resolved by a magnetic field. Using a fixed frequency and an increasing magnetic field, n electrons will give n transitions but in the absence of zero field splitting these transitions are coincident in energy and only one peak will be observed (e.g. Ni^{2+} in MgO). In the presence of zero-field splitting all transitions are observed (e.g. Cr^{+3}) (4).

When an electron interacts with a nucleus which possesses an angular momentum M_I (nuclear spin I), 2I + 1 orientations are possible and the main peak is split into 2I + 1 components. The selection rule is $M_I = 0$. This was first observed in $Cu(NH_4)_2(SO_4)_2.6H_2O$ (31) which gives four peaks because I for Cu^{65} and Cu^{63} is 3/2. In copperbissalicylaldimine each of the four components due to the interaction with the Cu nucleus is further split into 11 components due to the combined effect of the nitrogens (I = 1) and the protons (I = 1/2 giving rise to 44 peaks). The electron is delocalized on the ligand, which is good evidence for covalent bonding(25)

Several of the factors affecting line width in ESR are analogous to those in NMR. They include the following (2).

1) Spin-spin interaction is due to the mutual effect of one paramagnetic ion on the other. Each ion is regarded as a magnetic dipole which alters the magnetic field at the neighboring paramagnetic sites. (This effect can be reduced by moving the paramagnetic sites further apart, i.e. by diluting the salt with an isomorphous, diamagnetic equivalent). Similar effects can be produced by the magnetic dipole interaction with the protons of water molecules. For that reason sometimes crystals are grown from heavy water (13) because the deuterons have a magnetic dipole moment only about 1/3 of that of the protons.

2) Spin-lattice relaxation, occurs when the paramagnetic ions interact with the thermal vibrations of the lattice through spin-orbit coupling. Many measurements of relaxation time, however, give results inconsistent with this mechanism. Contrary to theory, it is found that relaxation times often do not vary inversely proportional to temperature and field strength and that they are sometimes dependent on crystal size (19). A lattice-bath relaxation time was proposed which represents the time required for the dissipation of energy to the crystal boundaries by the lattice modes.

3) Power saturation broadening occurs when the incident power is so large that the normal relaxation processes can no longer restore thermal equilibrium. In solid state ESR this effect is usually negligible.

4) Inhomogenous fields sometimes lead to broadening. In addition there is the effect of exchange which can easily be reduced by dilution of the crystals. The phenomenon of exchange is discussed more fully below.

$CuSO_4.5H_2O$ contains two types of Cu^{2+} ions per unit cell and hence we would expect to observe a peak corresponding to each. However at wavelengths shorter than about 8 cm. and at certain directions of the magnetic field only one peak is observed; in addition the peak is narrower than expected (10). Both phenomena are due to exchange interactions. When the external field H is along the tetragonal axis of one of the copper ions in a single crystal, the values of g, and therefore the precessional frequencies of the two ions are different. If there is an exchange between the ions, the absorption curve will depend on the magnitude of the exchange frequency relative to those of the precessional frequencies. When the former is large, a mean value of the energy of the copper ions is measured, and when it is smaller 2 lines appear (10, 20). The width of the line is a result of the precession of the magnetic moment which is under the influence of magnetic interactions which in turn are affected by non-magnetic effects such as exchange. When such atomic or electronic motions are rapid, the broadening effect of the magnetic interactions is reduced and "exchange narrowing" of the lines occurs (9).

Hydrated cupric acetate also contains two distinct ions per unit cell and one would therefore expect two lines each split into a quartet by interaction with the Cu nucleus. Instead a triply degenerate spin state results from exchange coupling, and one peak which is split into a septet due to the total nuclear spin of 3 is obtained(14). This is also observed in the propionate and butyrate but not in the formate (5). Solutions of copper complexes of monoethanolamine in alcohols give a spectrum of four hyperfine components as expected and in addition an exchange line superimposed, indicative of dimerization (28).

Solutions of $Cu(acac)_2$ (30) and $Cu(RR'NCS_2)_2$ (27) as well as other complexes give four lines of equal area but with line widths increasing with increasing I. These observations suggest that if the paramagnetic relaxation time (spin-spin as well as spin-lattice) depends on the nuclear orientation the hyperfine interactions contribute to the paramagnetic relaxation (26). McConnell(26) has derived expressions for the relaxation times which give reasonable agreement with experimental values. Recent work (29) has shown that the asymmetry of the spectrum was augmented with increase in viscosity and , the resonance frequency, in direct contradiction with McConnel's theory.

Only when the applied field is much stronger than the magnetic field due to the surroundings of the ion, are the hyperfine splittings equally spaced. When the two become of comparable magnitude the hyperfine levels will contain admixtures of the different quantum states M_I, which will give rise to unequal spacings. If the nucleus has a quadrupole moment additional peaks are observed; this effect is greatest when the applied field is at right angles to the crystalline field because both are trying to quantize the nucleus along their own axis. The result is that the selection rule $M_I = 0$ breaks down and sometimes nuclear quadrupole transitions are observed in addition to unequal spacing of the lines. When the effect of the quadrupole moment is comparable in magnitude to the nuclear interaction, 6I-1 lines result (11) as in the case of $(Zn, Cu)(NH_4)_2(SO_4)_2.6H_2O$ (21). An example of transitions forbidden by the $M_I = 0$ selection rule is $CuK_2(SO_4)_2.6D_2O$ (13).

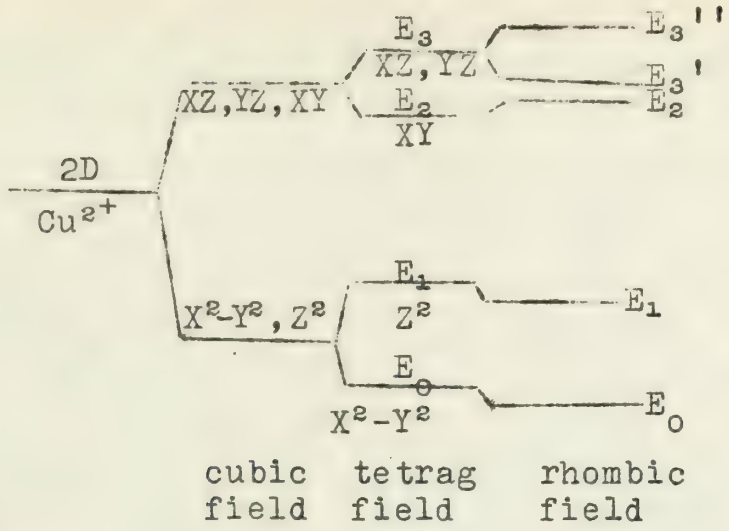
If a paramagnetic ion is located in a perfectly octahedral crystal site, the g-value is independent of the orientation of the single crystal in the magnetic field and is said to be isotropic. When the crystal field is tetragonal the g-value in the Z direction, g_Z, is different from the values in the X and Y directions g_X and g_Y and the g-values are anisotropic. The Z direction is defined as the highest-fold rotation axis which must be determined by x-ray methods. In a tetragonal field $g_Z \equiv g_{\parallel}$, the g-value with the external field parallel to the Z axis and $g_X = g_Y \equiv g_{\perp}$, the g-value with the field parallel to the XY plane. If θ is the angle between the magnetic field and the z-axis, the following relationship holds: $g^2 = g_{\parallel}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta$. If further distortion takes place, such as a rhombic one, g_X is no longer equal to g_Y and $g_{\perp}$ is without meaning. Small symmetry distortions which remain undetected by x-ray methods can thus be determined.

Taking into account the nuclear and quadrupole moment interactions and the anisotropy of the g-values, the Hamiltonian for an ion in a tetragonal environment becomes (excluding $W_F + V + W_{is}$) (6):

$$W = D[S_{Z^2} - 1/3\, S(S+1)] + g_{\parallel} H_Z S_Z + g_{\perp}(H_X S_Y + H_Y S_Y) +$$
$$A\, S_Z I_Z + B(S_X I_X + S_Y I_Y) + Q[(I_Z^2 - 1/3\, I(I+1)] - \gamma\beta_N HI$$

when S_X, S_Y and S_Z and I_X, I_Y and I_Z are the X, Y, Z components of the angular momenta of the electron and nucleus resp. D is the spin-spin splitting constant, A and B are the hyperfine splitting constants and Q the quadrupole constant; the term in D drops out for Cu^{2+} because $S_Z^2 = 1/4$ and $S = 1/2$; the last term is usually negligible. Given enough information the constants can, at least in principle, be evaluated. They can be calculated from experimental data but their signs are often difficult to determine. Some typical values for $CuSO_4.K_2SO_4.6H_2O$ are (7): $g_{\parallel} = 2.4$ $g_{\perp} = 2.1$

$|A| = 0.013\ cm^{-1}$ $|B| = 3.5 \times 10^{-3}\ cm^{-1}$ $|Q| = 0.9 \times 10^{-3}\ cm^{-1}$



The expression for the g-values (see figure) are:

$$g_{\parallel} = 2 - \frac{8\lambda}{E_2 - E_0} \qquad g_{\perp} = 2 - \frac{2\lambda}{E_3 - E_0}$$

where λ is the spin-orbit coupling constant and the values for the energy differences are obtained from the absorption spectrum. From experiment it is found that $g_X \neq g_Y$, which indicates that there is a small rhombic distortion. If a value is estimated for $E_3''-E_3'$, the agreement with experiment is reasonable (7) but it can be improved by taking values for λ different from the free ion value determined from atomic spectra: $\lambda = 828.7\ cm^{-1}$. For Cu^{2+} in water $\lambda = 710\ cm^{-1}$ (15) and for $Cu(NH_3)_4SO_4.H_2O$, $\lambda = 450\ cm^{-1}$ (18) as a rough estimate.

The calculated values for the hyperfine splitting constants A and B are in complete disagreement with experiment. It is known from optical spectroscopy that configurations with unpaired s electrons have a wider hyperfine structure. A new wavefunction is assumed which has admixtures of the configuration $[3S, 4S(^3S), 3d^9(^2D)]^2D$ expressed in terms of κ, which is a numerical factor expressing the admixture of configurations with unpaired s electrons (6,7,8). For $CuSiF_6.6H_2O$ a value of $\kappa = 0.30$ gives good agreement with experiment; this corresponds to a probability of only 4×10^{-5} for the configuration with the unpaired s-electron (6). The observation of forbidden transitions in later experiments with Cu Tutton salts made possible the determination of the signs of the hyperfine splitting constants and very accurate values for the quadrupole moments could be obtained (16).

For (Cu, Zn) $SiF_6.6H_2O$ the spectrum above 90°K consists of one band with partly resolved hyperfine structure. In the region of 90-20°K a transition takes place and at 20°K the spectrum consists of 3 sets of lines (12). The trigonal symmetry of the crystal leaves the ground state doubly degenerate. There are three

possible tetragonal Jahn-Teller distortions along the principal axes which lead to the same lowering in energy. The system may resonate among these three structures which leads to nearly isotropic g-values. At lower temperature the system no longer resonates and three lines with anisotropic g-values are observed(17).

In copper chelate complexes such as coppersalicylaldimine and $Cu(acac)_2$ appreciable covalent bonding occurs. The theory for the nearly ionic case discussed above is no longer valid and a molecular orbital model has to be used. The degree of mixing of metal orbitals and ligand orbitals is expressed by the constants α, β and β_1, with values ranging from 0.5 for the completely covalent to 1.0 for the completely ionic case. α describes the σ-bonding and β_1, and β the "in plane" and "out of plane" π bonding resp., the plane being that of the Cu nucleus and the chelate ring (24). For coppersalicylaldimine the values are $\alpha^2 = 0.83$, $\beta^2 \geq 0.91$ and $\beta_1^2 = 0.72$; the degree of π bonding in the plane is considerably greater than that out of the plane (25) Kivelson and Neiman(22) have summarized values for α and β, for a large number of Cu chelates. The values for α^2(0.75-0.90) indicate a large degree of covalent σ-bonding.

It is clear that a great deal of information can be gained from ESR experiments with regard to structure and bonding; many other examples could be cited. In order to carry out studies on single crystals, for which case the theory has been worked out in the greatest detail, one needs to know the crystal structure in order to know the orientation of the crystal in the field.

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N.M.R. IN THE PRESENCE OF PARAMAGNETIC IONS

Brad Wayland April 16, 1963

Paramagnetic species in the vicinity of a magnetic nucleus cause both relaxation and chemical shift effects. Relaxation studies have been most effective in yielding information on water exchange rates in dilute solutions of paramagnetic metal ions. Chemical shift effects have been used primarily in studying electron delocalization in paramagnetic complexes of conjugated ligands.

I. EFFECTS OF PARAMAGNETIC IONS ON THE RELAXATION TIMES OF MAGNETIC NUCLEI IN SOLUTION

Relaxation times of water protons in dilute aqueous solutions of paramagnetic ions have been extensively studied(1, 2). The addition of paramagnetic ions to water shortens the proton longitudinal (spin lattice) and the transverse (spin spin) relaxation times, T_1 and T_2 (3). The most successful correlation of experimental results has been achieved through consideration of both proton spin-electron spin dipole dipole interactions as formulated by Solomon (4), and proton spin-electron spin exchange coupling as suggested by Bloembergen (5). The dipolar term arises from the flucuating magnetic field created by the tumbling paramagnetic ion. The magnetic moment of an unpaired electron is $\sim 10^3$ times larger than the nuclear magnetic moment and thus the electron-nuclear dipole term dominates over the nuclear-nuclear dipole term. If the unpaired electron has a wave function which has a finite probability at the magnetic nucleus then the Hamiltonian contains an electron spin-nuclear spin coupling term of the form AI·S. This mechanism may also produce a fluctuating magnetic field at the nucleus and shorten T_1. Also, if the lifetime of the paramagnetic state is long then a distribution of fields results which shortens T_2, but has little effect on T_1.

The electron spin-nuclear spin dipolar and exchange coupling interactions are given by the Hamiltonians (1) and (2) respectively:(6)

$$(1) \quad H_1 = \frac{\hbar^2 \gamma_I \gamma_S}{r^3} \left[3(I\cdot r)(S\cdot r) - I\cdot S\right]$$

$$(2) \quad H_2 = AI\cdot S$$

The combined Solomon-Bloembergen equations for T_1 and T_2 appear in a simplified form as equations 3 and 4.

$$(3) \quad \frac{1}{T_1} = \frac{1}{T_1\,\mathrm{dip}} + \frac{1}{T_1\,\mathrm{ex.}} = \frac{4}{30}\,\frac{S(S+1)g^2\gamma_I^2\beta^2 P}{r^6}\left[3\tau_c + \frac{7\tau_c}{1+\omega_S^2\tau_c^2}\right] + \frac{2}{3}\,\frac{S(S+1)A^2P}{\hbar^2}\,\frac{\tau_e}{1+\omega_S^2\tau_e^2}$$

$$(4)\quad \frac{1}{T_2} = \frac{1}{T_2}\,\text{dip} + \frac{1}{T_2}\,\text{ex.} = \frac{4}{60}\,\frac{S(S+1)g^2\gamma_I^2\beta^2P}{r^6}\left[7\tau_C + \frac{13\tau_C}{1+\omega_S^2\tau_C^2}\right] + \frac{1}{3}\,\frac{S(S+1)A^2P}{\hbar^2}\left[\tau_e + \frac{\tau_e}{1+\omega_S^2\tau_e^2}\right]$$

γ_I = gyromagnetic ratio β = Bohr magneton

A = coupling constant for exchange interaction

P = probability of finding a given proton in the hydration sphere of the paramagnetic ion and is proportional to the metal ion concentration

τ_C = correlation time for dipolar relaxation

τ_e = a measure of the lifetime of the paramagnetic state

ω_S = Larmor frequency for the electron

$$(5)\quad \frac{1}{\tau_e} = \frac{1}{\tau_S} + \frac{1}{\tau_h}$$

τ_S = electron relaxation time - a measure of the lifetime of an electron spin state

τ_h = chemical exchange time for protons in the solvation sphere

$$(6)\quad \frac{1}{\tau_c} = \frac{1}{\tau_s} + \frac{1}{\tau_r}$$

τ_r = correlation time for tumbling of the hydrated magnetic ion.

The important features to recognize in equations (3) and (4) are;

Case 1: If $\omega_S^2\tau_e^2 \ll 1$ (i.e. τ_S is very short) then $T_1=T_2$ and T_1 may be relatively long (10^{-1} -10^{-3} sec) so that the N.M.R. spectra is not appreciably broadened.

Case 2: If $\omega_S^2\tau_e^2 \gg 1$ (i.e. τ_S is very long) then $T_1 \gg T_2$ and the NMR spectra is extensively broadened due to exchange coupling.

Most paramagnetic metal ions have short electron spin relaxation times ($\tau_S = 10^{-10}$-10^{-12} sec.) in aqueous solutions and belong to case 1. The ions Mn^{+2}, Gd^{+3} and Fe^{+3} with half filled shells (S states) have relatively long spin relaxation times ($\tau_S \geq 10^{-8}$-10^{-9} sec) because spin orbit coupling and distortion of the hydration sphere are minimized and are examples of case 2 (5, 7). However, when Mn^{+2} is complexed by EDTA in aqueous solution τ_S is appreciably shortened and $T_1=T_2$ (8, 9). Thus Mn^{+2} when complexed with EDTA becomes an example of case 1.

Connick (1), following the proton experiments of Gutowsky et. al., (6) has used temperature dependence of T_2 in studying the water exchange rates of paramagnetic ions by O^{17} nuclear resonance. The general expression for T_2 given by equation 7 was achieved

by analysis of the Bloch equations modified for chemical exchange between a diamagnetic and a paramagnetic site (1, 10, 11).

$$(7)\quad \frac{1}{T_{2P}} = \frac{1}{T_2} - \frac{1}{T_{2A}} = \frac{1}{\tau_A}\left[\frac{T_{2B}^{-2} + T_{2B}^{-1}\,\tau_B^{-1} + \Delta\omega_B^2}{(T_{2B}^{-1} + \tau_B^{-1})^2 + \Delta\omega_B^2}\right]$$

T_{2P} ≡ transverse relaxation due to the paramagnetic ion

T_2 ≡ transverse relaxation time

τ_A ≡ lifetime of the magnetic nucleus in the diamagnetic site

τ_B ≡ lifetime of the magnetic nucleus in the paramagnetic site

T_{2A} ≡ transverse relaxation time in the diamagnetic site

T_{2B} ≡ transverse relaxation time in the paramagnetic site

$\Delta\omega_B$ ≡ difference in the Larmor frequency between the diamagnetic and paramagnetic sites

The temperature dependence of equation 7 was investigated for the following limiting cases:

$$(7A)\quad \Delta\omega_B^2 \ll \frac{1}{T_{2B}},\ \frac{1}{\tau_B}$$

Equation 7 becomes:

$$\frac{1}{T_{2P}} = \frac{P_B}{\tau_B} = \frac{1}{\tau_A}$$

Relaxation occurs through a change in the precessional frequency and is rapid. $\frac{1}{T_{2P}}$ is controlled by the rate of water exchange.

$$(7B)\quad \frac{1}{\tau_B^2} \gg \Delta\omega_B^2 \gg \frac{1}{T_{2B}\ \tau_B}$$

$$\frac{1}{T_{2P}} = P_B\,\tau_B\,\Delta\omega_B^2$$

Chemical exchange is rapid. $\frac{1}{T_{2P}}$ is controlled by the rate of relaxation through change in precessional frequency.

$$(7C)\quad \frac{1}{T_{2B}^2} \gg \Delta\omega_B^2,\ \frac{1}{\tau_B^2}$$

$$\frac{1}{T_{2P}} = \frac{P_B}{\tau_B} = \frac{1}{\tau_A}$$

Relaxation by T_{2B} is fast. $\frac{1}{T_{2P}}$ is controlled by the rate of water exchange.

$$(7D)\quad \frac{1}{T_{2B}\,\tau_B} \gg \frac{1}{T_{2B}^2}\,,\quad \tau_B^2$$

$$\frac{1}{T_{2P}} = \frac{P_B}{T_{2B}}$$

Chemical exchange is rapid. $\frac{1}{T_{2P}}$ is controlled by the T_{2B} relaxation process.

A detailed analysis of the temperature dependence of T_2 for aqueous solutions of Mn^{+2} will be given to demonstrate the evaluation of water exchange rates.

FIGURE 1

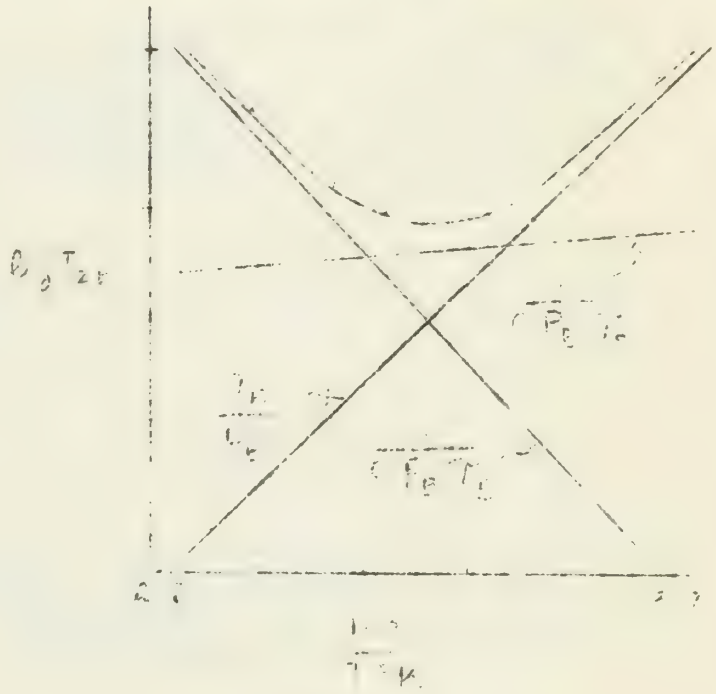


FIGURE 2

From figure 1 it is seen that $\frac{T_1}{T_2} \gg 1$ and thus $\tau_S^2\,\omega_e^2 \gg 1$. Equation 4 reduces to the form:

$$(8)\quad \frac{1}{T_{2B}} = C\,\tau_e \qquad \frac{1}{\tau_e} = \frac{1}{\tau_S} + \frac{1}{\tau_B}$$

At high temperatures T_{2B} is controlled by chemical exchange (τ_B), while at lower temperatures the electronic interruption (τ_S) will dominate T_{2B}. $\frac{1}{\tau_B}$ is the rate of a chemical reaction and should follow an exponential temperature dependence.

$$(9)\quad \frac{1}{\tau_B} = \left(\frac{kT}{h}\right)^{-1} e^{(\Delta H^{+}/RT - \Delta S^{+}/R)}$$

The temperature dependences of τ_e and τ_S are given by equations 10 and 11.

$$(10)\quad \frac{\Delta\omega}{\omega} = \frac{4}{9}\,\frac{A\gamma_e}{\tau_P}\,\frac{I(I+1)(S)S+1)}{kT}$$

$$(11)\quad \frac{1}{\tau_S} = \frac{12\,C_2^2}{5\hbar^2 S(S+1)}\;\frac{\tau_v}{1+\omega_S^2\tau_v^2} + \frac{4\tau_v}{1+\omega_S^2\tau_v^2}$$

$\tau_v \equiv$ correlation time for collision of water molecules with the hydrated ion.

$\tau_v \equiv \tau_v^{\circ}\; e^{\Delta v/RT}$

The plot of log T_{2P} versus $\frac{1}{T^{\circ}K}$ given in figure 2 reveals that a low temperatures T_{2P} is controlled by chemical exchange corresponding to equation 7A or 7C. An estimate of τ_B from the low temperature slope eliminated the possibility of ω effecting the relaxation because an impossibly high coupling constant would be necessary to explain the data. When ω is very small equation 7 reduces is equation 12.

$$(12)\quad \frac{1}{T_{2P}} = \frac{(\tau_A T_{2B})^{-1}}{T_{2B}^{-1} + \tau_B^{-1}} = \frac{P_B}{\tau_B + T_{2B}} = \frac{P_B}{\tau_B = \frac{1}{C}\left(\frac{1}{\tau_S} + \frac{1}{\tau_B}\right)}$$

$$\frac{\tau_A}{\tau_B} = \frac{P_A}{P_B} \qquad P_A \cong 1 \qquad \tau_A = \frac{P_A}{P_B}\tau_B = \frac{\tau_B}{P_B}$$

The solid curve in figure 2 which passes through the experimental points was calculated as the sum of three lines derived for the cases of high, low and intermediate temperature. At low temperature $\tau_B \gg \frac{1}{C}\left(\frac{1}{\tau_S} + \frac{1}{\tau_B}\right)$ and $T_{2P} = \frac{\tau_B}{P_B}$. At high temperatures $\frac{1}{\tau_B} \gg \frac{1}{\tau_S}$ and τ_B and $T_{2P} = \frac{1}{CP_B\tau_B}$. At intermediate temperatures τ_s contributes appreciably to T_{2P} and $T_{2P} = \frac{1}{CP_B\tau_S}$. By using a curve fitting process parameters for the exchange process were determined (Table 1).

TABLE 1: Values for the exchange of H_2O from the first coordination sphere of Mn^{+2} ion.

	O^{17}	proton(6)	proton(2)
$\Delta H^{\ddagger}$ k cal	8.1	7.8	7.5
k_1 (sec^{-1} at 298°K)	3.1×10^7	3.6×10^7	4.0×10^7
τ_S (sec at 298°K)	3.8×10^{-9}	3.0×10^{-9}	3.5×10^{-9}
A/h (c.p.s)	2.7×10^6	1×10^6	1.0×10^6
$\Delta S^{\ddagger}$ (eu)	2.9	2.2	1.3

Connick has also determined water exchange parameters for Cu^{+2}, Fe^{+2}, Ni^{+2} and Co^{+2} in dilute aqueous solution (Table 2). The temperature dependence of T_{2P} takes several different forms for this series of metal ions. In each case, however, a term involving water exchange was involved which allowed exchange data to be determined. Similar exchange experiments have been carried out on exchange of NH_3 and Cl^- in aqueous solution by observing the N^{14} and $Cl^{35,37}$ nuclear resonance (12, 13).

TABLE 2: Values for exchange of H_2O from the first coordination sphere of Cu^{+2}, Mn^{+2}, Fe^{+2}, Co^{+2} and Ni^{+2}

	Cu^{+2}	Mn^{+2}	Fe^{+2}	Co^{+2}	Ni^{+2}
ΔH^{+}(k.cal.)	11	8.1	7.7	8.0	11.6
k_1 (sec^{-1})	1.0×10^4	3.1×10^7	3.2×10^6	1.13×10^6	2.7×10^4
τ_S (sec)		3.8×10^{-9}	1.4×10^{-11}	5×10^{-12}	1.3×10^{-11}
A/h(c.p.s.)	5.5×10^5	2.7×10^6	9.8×10^5	1.14×10^6	3.6×10^6
ΔS^{+}(eu)	-4.0	2.9	-3.0	-4.1	0.6

II. PROTON CHEMICAL SHIFTS AND CARBON SPIN DENSITIES OF CONJUGATED LIGANDS BONDED TO PARAMAGNETIC IONS

Large proton chemical shifts have been reported for some paramagnetic acetylacetonates (14), metalocenes(15-17), and for a wide variety of Ni(II) chelates of N,N' disubstituted amino-troponeimines(18-23). Commonly the proton shifts are in the range from +5000 c.p.s. to -5000 c.p.s. using a 40 Mc. probe. These shifts are a full order of magnitude larger than shifts observed for protons in diamagnetic species.

These large contact proton NMR shifts can be visualized as resulting from the unpairing of ligand electron pairs due to charge transfer to the paramagnetic metal ion. The effects of the unpaired electron in the ligand π orbitals must be transferred to the protons via the Fermi Contact term (24), for the dipolar interactions average to zero due to rapid molecular tumbling in solution. The observed nuclear spin-electron spin coupling must arise from π - σ exchange coupling (appendix I) in order to place a finite odd electron density at the in plane aromatic protons(25,26). In a system characterized by a very short electron spin relaxation time or a short exchange time, the proton N sees a single average hyperfine magnetic field corresponding to the effective spin Hamiltonian for proton N, where $\langle S_Z \rangle$ is the time average value of the Z component of electron spin(27). Since γ_N is positive for the

$$(13) \quad H = -\gamma_{NZ} [H_o - 2\pi A_N \frac{I\hbar}{\gamma_N} \langle S_Z \rangle]$$

$$(14) \quad \langle S_Z \rangle = \frac{-g\beta S(S+1)H_o}{3kT}$$

$$(15)\quad H = -\mu_{NZ} H_o \left[1 - 2 A_N \frac{I\hbar}{\mu_N} \frac{g\beta S(S+1)}{3kT}\right]$$

μ_{NZ} ≡ Z component of the magnetic moment for proton N

A_N ≡ electron spin-nuclear spin contact interaction constant (coupling constant)

β ≡ Bohr magneton

proton equation 15 predicts that the contact shift will be to lower fields when A_N is positive and to higher fields when A_N is negative. It is apparent that N.M.R. offers a direct means of determining the sign of the electron spin-nuclear spin coupling constant.

Bloembergen (5) has explicitly formulated the relationship between the nuclear resonance contact shift and the scalar coupling constant (A_N) as equation 16.

$$(16)\quad \frac{\Delta H}{H} = \frac{\Delta\nu}{\nu} = - 4A_N \frac{\gamma_e}{\gamma_N} \frac{g\beta I(I+1)\, S(S+1)}{9kT}$$

Equation 17 is for the specific case of proton magnetic resonance.

$$(17)\quad \frac{\Delta H}{H} = \frac{\Delta\nu}{\nu} = - \frac{1}{3} A_N \frac{\gamma_e}{\gamma_e} \frac{g\beta S(S+1)}{kT}$$

γ_e ≡ magnetogyric ratio for the electron

γ_N ≡ " " " " magnetic nucleus

I ≡ nuclear spin

S ≡ electron spin multiplicity

ΔH ≡ $H_{complex} - H_{ligand}$

Contact interaction constants (A_N) are related to the unpaired spin densities on p_π orbitals of SP^2 carbons by equation 18 (28, 29, 30).

$$(18)\quad A_N = Q\rho_N$$

ρ_N ≡ spin density at carbon

Q = proportionality constant (-22.5 Gauss for an aromatic C-H fragment).

Spin density (ρ_N) is defined as that fraction of an unpaired electron which appears to be localized at site N. Spin densities may be either positive or negative. A negative spin density results when the electron spin at site N is antiparallel to the net spin of the paramagnetic species.

REQUIREMENTS FOR OBSERVATION OF A HYPERFINE CONTACT SHIFT

Conventionally spin density distributions have been obtained from the isotropic nucleus-electron hyperfine splittings that appear in EPR spectroscopy. Under special conditions spin densities are manifested in the NMR by large chemical shifts. NMR contact shifts have the advantage over EPR of offering a means of determining both the magnitude and the sign of the coupling constant and spin density. The conditions requisite to observing a contact shift in the NMR are that either of the inequalities (19) are satisfied(27).

$$(19) \quad \frac{1}{\tau_S} \gg A \qquad \frac{1}{\tau_e} \gg A$$

τ_S ≡ electronic relaxation time
τ_e ≡ chemical exchange time
A ≡ contact interaction constant (coupling constant)

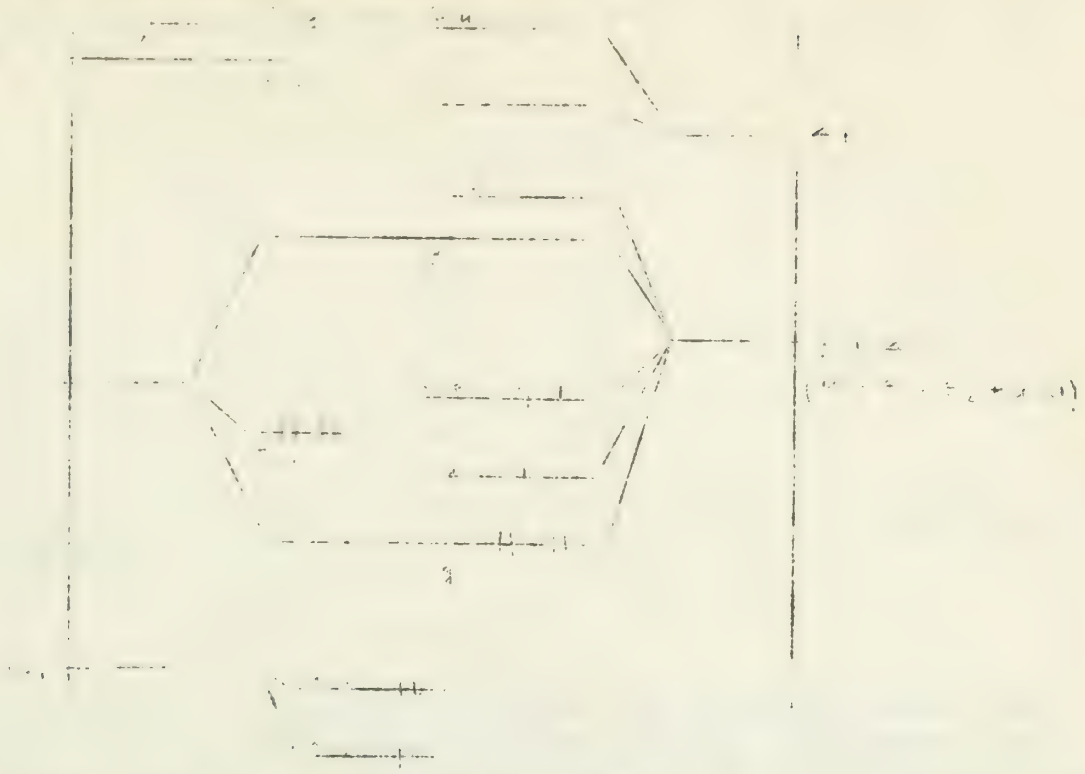
It is interesting to note that the conditions requisite to observing a sharp nuclear resonance spectrum imply the absence of observable hyperfine splittings for the same system in the EPR. If $\frac{1}{\tau_e} \gg A$, the hyperfine splittings are obscured by exchange narrowing, and if $\frac{1}{\tau_S} \gg A$ then the paramagnetic resonance line widths are greater than the splittings.

MECHANISM FOR PLACING AN UNPAIRED ELECTRON ON THE LIGAND BONDED TO A PARAMAGNETIC ION

The transference of effects of unpaired electrons on the metal ion to the ligand can be qualitatively explained by charge transfer from the ligand to the metal ion (16, 17, 31). The spin of the electron transferred is such that the multiplicity of the next lower oxidation state of the metal ion is achieved. The unpaired electron remaining on the ligand may thus have a spin parallel with or antiparallel to the net spin of the metal ion. Antiparallel spin on the ligand results most frequently for ions whose next lowest oxidation state has higher multiplicity. Spin parallel to the metal ion results when the next lower oxidation state has lower multiplicity. Before offering evidence for this mechanism, it is necessary to know that the unpaired spin density at the proton is antiparallel to the spin density at the carbon atom to which it is bonded. This effect arises from . - exchange interaction discussed more fully in appendix 1 (25-27).

The proton magnetic resonances of the bis-cyclopentadienyl compounds of V^{+2}, Cr^{+2}, Mn^{+2}, Co^{+2} and Ni^{+2} have been recorded(15-17). The vanadium and chromium compounds give proton resonance shifts to lower fields while the protons in the manganese, cobalt and nickel compounds are shifted to higher fields. $V(C_5H_5)_2$ will be considered in more detail in order to illustrate the mechanism for transferring unpaired spin to the ligand. Figure 3 is a molecular orbital diagram for metalocene compounds. The electrons

are assigned for the case of vanadocene.



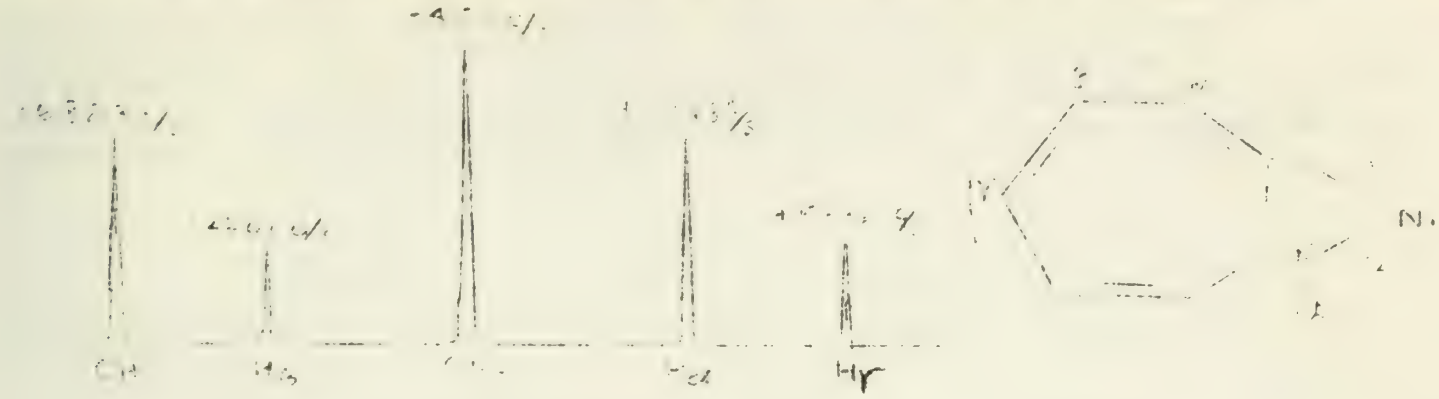
orbitals for 2 cyclopentadiene rings | metalocene orbitals | metal orbitals

FIGURE 3

The most important charge-transfer process involves electrons passing from the filled e_{1g} ring orbitals into the empty e_{1g} d orbital of the vanadium ion. The electron transferred has spin parallel to the spin of the metal ion for this leads to a favorable exchange energy. The electron transfer process essentially produces V^{+} ion with electron configuration $(a_{1g})^1(e_{2g})^1(e_{-2g})^1(e_{1g})^1$. The unpaired electron remaining on the ligand has spin antiparallel to the metal ion which places parallel unpaired spin at the proton. This mechanism predicts a proton shift to lower fields in agreement with experimental results. The Ni^{+2} ion in nicklocene is assigned the electronic configuration $(e_{2g})^4(a_{1g})^2(e_{1g})^2$. All of the d orbitals are either filled or half filled. The electron transferred from the ligand must have spin antiparallel to the d electrons. This process predicts a high field shift for the ligand protons in agreement with the observed shift.

In the above metallocene compounds the carbon spin densities in any one compound are found to have the same sign, for all of the carbons and protons are effectively equivalent. In ligands of lower symmetry where there are preferred positions for the unpaired electron, the spin density on adjacent atoms is found to alternate in sign. The preferred positions have spin parallel to the electron remaining on the ligand after charge transfer, while adjacent positions have unpaired spin antiparallel to the net spin of the ligand. This effect arises from $\pi - \pi$ configuration interaction(21,29) (Appendix 2). The preferred positions for the unpaired electron can

be predicted by considering the possible valence bond structures. Ni(II) N, N' diethylaminotroponeimineate serves as a good example(21).



Proton magnetic resonance spectra of Ni II N, N'diethylaminotroponeimineate

FIGURE 4

Valence bond structures (Figure 5) place the unpaired electron at the α and γ positions of the seven membered ring. No structure placing the odd electron at the β position can be written without recourse to long bonds. As in the case of nicklocene, the ligand

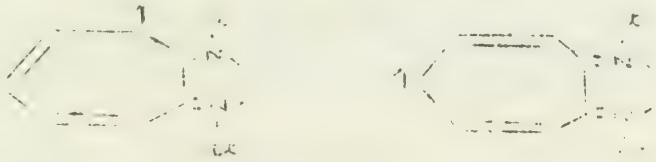


FIGURE 5

as a whole has spin parallel to the Ni ion. Positive spin densities are thus predicted for the α and γ carbons and a negative spin density is expected for the β carbon. Remembering that the spin density at the proton is antiparallel to that on the carbon, the α and γ protons are expected to be shielded while the β proton should be deshielded. These considerations lead immediately to the NMR assignment in Figure 4. Confirmation of the assignment in Figure 4 has been made by other independent means. Substitution of phenyl for ethyl on the nitrogens of the previous compound extends the π system over which the unpaired spin is distributed. As expected from simple valence bond consideration, (Figure 6) positive spin densities occur at the ortho and para positions and a negative spin density is found at the meta position.

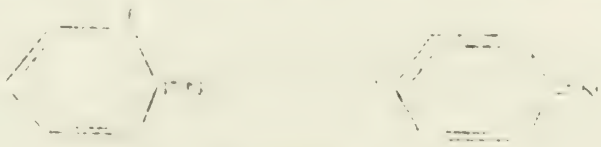
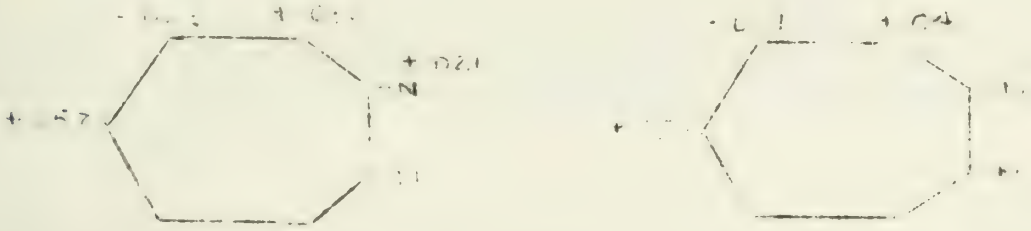


FIGURE 6

Valence bond calculations of spin densities by the method of McConnell(32) have been useful for predicting spin densities at atoms not readily observable in the NMR. The calculations are made assuming the ligand to be a free radical. The values obtained are then scaled down to correspond to the transfer of that fraction of an electron which best agrees with the observed spin densities. Example results given in Figure 7 are in amazingly good agreement with experiment. (21)



spin densities calculated for transfer of .10 electrons

experimental spin densities

FIGURE 7

It is apparent that NMR spin density determinations provide a promising new approach to the study of conjugation in molecules containing extended π electron systems. The ability of NH, O, S, and $-SO_2$ groups to transfer electronic effects has been directly studied using this technique (21). The importance of F double bonding with π systems has also been assesed(20).

Contact shifts due to paramagnetic ions are not limited to conjugated ligands. Fluorine NMR of paramagnetic crystals has demonstrated the presence of large internal magnetic fields at the fluorine nucleus (33-36). Isotropic hyperfine interactions arise from the unpairing of 2S electrons. A smaller anisotropic effect is caused by the unpairing of 2P electrons. Single crystal fluorine NMR of $KMnF_3$ has yielded information on antiferromagnetic ordering in the solid state (37). O^{17} NMR of aqueous solutions of rare earth perchlorates has been reported (38). The observed magnitude and variation of the O^{17} contact shifts with the number of 4f electrons was interpreted as evidence for very weak covalent bonding between O^{17} 2S and 2P orbitals with the rare earth 6S orbitals. The 4f, 5d, and 6p orbitals play at most a minor role in the bonding.

APPENDIX 1

π - σ Transmission of Spin Polarization Through Exchange Coupling in the C-H Fragment

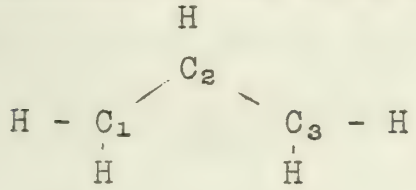
The theory of π - σ exchange coupling has been worked out in order to explain the presence and direction of spin polarization at the protons in paramagnetic complexes of conjugated ligands (25, 26). An orthogonal basis set was chosen for the calculation. If the unpaired electron is placed in a π M.O. of the aromatic ligand, then there is zero electron density at the inplane aromatic protons. An excited electronic configuration must be used to give rise to the

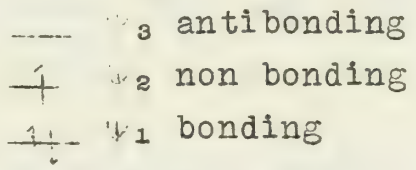
indirect coupling. The lowest energy excited configuration which gives the proper result is the excitation of one electron from a σ_B bonding orbital to a σ antibonding orbital. Linear combinations of Slater determinants are made in order to produce proper eigenfunctions for the possible excited states. The doublet excited state corresponding to a triplet $_B$ $_A$ with the π electron opposite in spin leads the proper interaction. The excited state which mixes with the ground state always places spin polarization at the proton which is antiparallel to the spin of the π electron. An alternate and probably more realistic approach to this problem can be made by simply assuming that the π and σ orbitals are not orthogonal. Spin exchange may thus directly occur which places spin density at the proton antiparallel to the unpaired electron in the π system.

APPENDIX 2

π - π Configuration Interaction

Negative spin density is a concept foreign to molecular orbital theory. M. O. theory must be modified by addition of π - π configuration interaction in order to account for negative spin densities. Configuration interaction is the unpairing of electron spins so as to reduce the energy of the system through exchange of electrons having the same spin. The allyl free radical will be briefly discussed in order to demonstrate the effects of configuration interaction on the spin densities of conjugated radicals (21).





The odd electron in ψ_2 gives rise to positive spin densities at carbons 1 and 3. Exchange interactions between the odd electron in ψ_2 of spin α and the paired electron in ψ_1 of spin β enhances the positive spin density at C_1 and C_3 and leaves a net spin β (negative spin density) at C_2. This effect is also responsible for producing negative spin densities near the nucleus of many paramagnetic metal ions (35).

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AQUEOUS INFRARED SPECTROSCOPY AND ITS APPLICATIONS TO INORGANIC CHEMISTRY

Ronald H. Carlson April 23, 1963

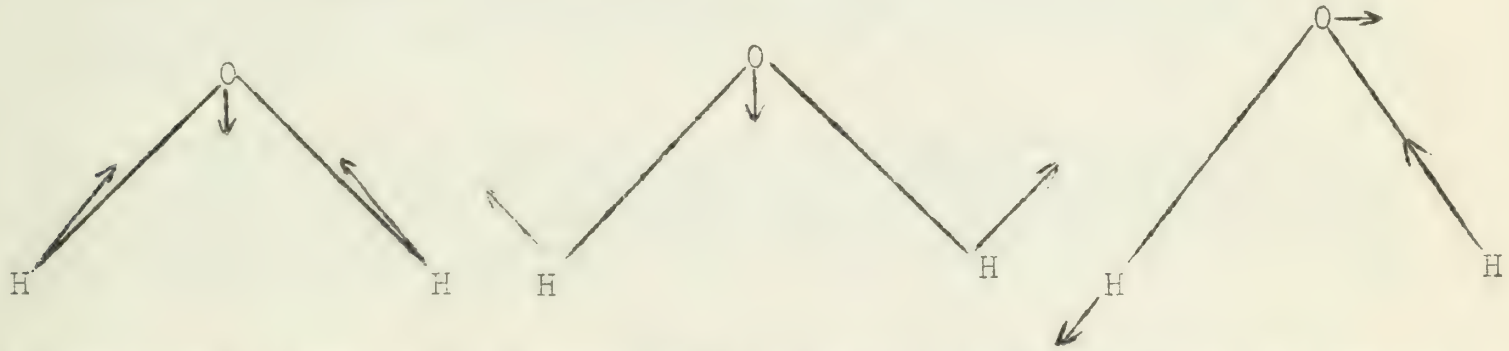
INTRODUCTION

Water has generally been recognized as being a very poor infrared solvent. However, with the advent of the modern double beam spectrophotometer and with the development of suitable optical materials for use as infrared cell windows, aqueous infrared spectroscopy has rapidly become an important tool for the investigation of many inorganic and biological systems.

Coblentz (1) was the first to show that H_2O can be used as an infrared solvent. More recently, Gore and coworkers (2) have shown that H_2O, when used in conjunction with D_2O, can be extremely useful in this respect. The field of aqueous infrared spectroscopy was not extensively pursued until about 1953 when Blout and Lenormant (3) published some infrared spectra of biologically important materials in H_2O and D_2O. Since then, interest in this field has grown considerably and the number of applications is increasing.

THEORY AND EXPERIMENTAL

Water is a nonlinear triatomic molecule and as such should show 3N-6=3 normal modes of vibration. The normal modes of vibration of H_2O, along with their symmetry classifications and absorption frequencies are (4):



A_1 (symmetric stretch) ν_1= 3651cm.$^{-1}$ (vapor) A_1 (symmetric deformation) ν_2= 1595cm.$^{-1}$ (vapor) B_1 (asymmetric stretch) ν_3= 3755cm.$^{-1}$ (vapor)

The corresponding normal modes of vibration of D_2O and HDO vapor have absorbance frequencies of ν_1=2666cm^{-1}, ν_2=1178cm.$^{-1}$, ν_3=2789cm.$^{-1}$ and ν_1=2719cm.$^{-1}$, ν_2=1402cm.$^{-1}$, ν_3=(overlapped by ν_3 of H_2O), respectively.

In <u>liquid</u> H_2O, the aforementioned absorption bands are broadened out considerably, with the result that there is an almost continuous absorption over the entire rock salt region. There are, however, two "windows" in this region where water is reasonably transparent; these are from 3.5μ to 5.8μ (2860 cm.$^{-1}$ to 1730 cm.$^{-1}$) and from 6.5μ to 10.5μ (1540 cm.$^{-1}$ to 955 cm.$^{-1}$). It is generally agreed that hydrogen bonding is the principal cause

for the intense infrared absorption of water, since perturbations by neighboring molecules are regarded as a prime factor in producing line broadening in liquids (5). The compound D_2O is quite a bit more transparent than H_2O and exhibits windows in the rock salt region from 2.5μ to 3.6μ (4000 cm.$^{-1}$ to 2780 cm.$^{-1}$), 4.8μ to 7.8μ (2080 cm.$^{-1}$ to 1280 cm.$^{-1}$), and 8.7μ to 13.3μ (1150 cm.$^{-1}$ to 750 cm.$^{-1}$). Thus it can be seen that H_2O, when used in conjunction with D_2O, is a fairly transparent infrared solvent and as such enables one to obtain a spectrum over the entire rock salt region.

One of major experimental difficulties encountered in the use of aqueous infrared spectroscopy is the need to use very short path lengths and, consequently, fairly concentrated solutions in order to obtain appreciable solute absorption. The longest path lengths that can conveniently be used in this regard are of the order of 0.075 mm (6). Path lengths of the order of 0.025 mm are usually employed in most infrared cells for optimum results. This thickness of water, small though it may seem, transmits only a small percentage of the incident radiation at 1100 cm.$^{-1}$. Therefore, fairly large slit widths are required in order to insure that a sufficient amount of energy reaches the detector. Operating at large slit widths leads to a loss in resolution of the spectrum However, infrared bands in aqueous solution are usually so broad that a high degree of resolution is not necessary. The limit imposed by aqueous solutions upon the cell path length requires that a material have a solubility of at least 1% in H_2O in order to produce a spectrum. The infrared spectrum of more difficultly soluble materials can nonetheless be obtained through use of an ordinate scale expansion attachment available with most modern spectrophotometers. This attachment allows the spectroscopist to expand an infrared band up to ten times its normal height, and thus record the spectra of difficultly soluble materials the spectra of which under normal conditions would be extremely weak and distorted.

Another major difficulty encountered in aqueous infrared spectroscopy lies in the selection of suitable materials for cell windows which are both resistant to H_2O and transparent to infrared radiation. Table I lists some optical materials which can be used as cell windows (7,8).

Table I

Material	Limit of Transmission (from UV)	
	μ	Cm.$^{-1}$
fused quartz	4	2500
sapphire	6	1670
LiF	7	1430
CaF_2	10	1000
BaF_2	13	770
As_2S_3	12.5	800
KRS-5(TlBr,I)	35	285
Kodak I.R. Trans.	14	715
Kodak 80-20 (As modified Se glass)	25	400
AgCl	28	355

One of the more useful window materials for the construction of fixed thickness cells is BaF_2 since it is transparent over practically the entire rock salt region and is quite resistant to water. Plates of BaF_2 are, however, readily attacked by strongly acidic solutions and are very fragile. Cells constructed from this material must, therefore, be used with extreme care. Fixed-thickness AgCl cells find considerable use in investigations of highly acidic solutions where use of BaF_2 cells is not practical. Kodak "I. R. Trans" plates are extremely valuable in obtaining qualitative identification spectra where the need for a fixed thickness cell does not arise. Usually only one drop of solution is required in using the "I. R. Trans" plates.

Adequate compensation for residual solvent absorption in any one of the window regions of H_2O or D_2O can be obtained by placing a second absorption cell containing pure solvent into the reference beam of the spectrophotometer. The sample and reference cells should be of the same path length in order to insure maximum compensation. Another method of compensating for solvent absorption is to insert a transmittance screen or optical attenuator into the reference beam (9).

APPLICATIONS

(1) Qualitative identification of molecules in solution

One of the widest applications of aqueous infrared spectroscopy to date has been in the identification and examination of many biologically important systems. Aqueous media provide a natural physiological environment for such systems, and hence a study of their infrared spectra in this natural environment can be most rewarding. A good review of some biological systems which have been investigated by aqueous infrared techniques is offered by Parker (10).

The infrared spectra of several inorganic acids have been recorded both in H_2O and in D_2O, and the existence of discrete H_3O^+ ions in the liquid state has been confirmed (11). Three absorption bands were observed in the spectrum of each acid corresponding to the six normal modes of vibration of H_3O^+. The similarity between these spectra and that of isoelectronic NH_3 was taken as sufficient proof that a true chemical bond between the proton and one of the adjacent water molecules exists long enough for the resulting species to undergo normal vibrations. Evidence regarding the degree of ionization of these acids was obtained through spectroscopic observation of the relative concentration of H_3O^+ existing in solution.

(2) Molecular structure as a function of pH

Aqueous amino acids exhibit a molecular structure which depends upon the pH of the solution in which the amino acid is dissolved. In highly acidic media, amino acids exist in a

cationic form, whereas in neutral media they exist as dipolar ions or "zwitterions", and in basic media they exist in an anionic form. The ionization scheme for an amino acid can be represented by the following, using glycine as an example:

$$\underset{\text{Cation}}{\overset{+}{NH_3}\text{-}CH_2\text{-}COOH} \underset{DCl}{\overset{HCl}{\rightleftharpoons}} \underset{\text{Zwitterion}}{\overset{+}{NH_3}\text{-}CH_2\text{-}COO^-} \underset{NaOD}{\overset{NaOH}{\rightleftharpoons}} \underset{\text{Anion}}{NH_2\text{-}CH_2\text{-}COO^-}$$

Infrared spectroscopy is remarkably well adapted for following the attendant structural changes in aqueous amino acids as a function of pH (2,12). The <u>unionized</u> carboxyl group of the <u>cation</u> gives a characteristic absorption in D_2O at approximately 1740 cm.$^{-1}$, whereas the <u>ionized</u> carboxylate group of the <u>zwitterion</u> gives a characteristic absorption in D_2O at approximately 1610 cm.$^{-1}$, and the <u>ionized</u> carboxylate group of the <u>anion</u> gives a characteristic absorption at approximately 1580 to 1590 cm.$^{-1}$ in D_2O. Since each of the three structural forms of an amino acid has a characteristic carboxyl(ate) frequency associated with it, it is very easy to ascertain which species is predominant in solution at a given pH by noting the position and relative intensity of the respective carboxyl(ate) bands.

Martell and coworkers (13, 14) used infrared spectroscopy in an investigation of the molecular structure of nitrogen containing polycarboxylic acid ligands as a function of pH. Among the ligands which were studied were iminodiacetic acid (IMDA), nitrilotriacetic acid (NTA), and ethylenediaminetetraacetic acid (EDTA). The criterion used for structural identification as a function of pH was the same as that used in the case of simple amino acids, namely the position and relative intensity of the asymmetric carboxyl(ate) stretching band. In these amino-acid type systems, three carboxyl(ate) asymmetric stretching bands can be distinguished: type (A), un-ionized carboxyl band; type (B), α-<u>ammonium</u> carboxylate ($R_2\overset{+}{N}HCH_2COO^-$) band; and type (C), α-<u>amino</u> carboxylate ($R_2NCH_2COO^-$) band. The type A bands absorb at 1700~1730 cm.$^{-1}$ and have an extinction coefficient roughly one-third that of the type B and C bands, which absorb at 1620~1630 cm.$^{-1}$ and 1575~1585 cm.$^{-1}$, respectively. The results obtained by Martell and coworkers are summarized in Table II. Chapman and coworkers (15) and Sawyer and Tackett (16) have investigated the aqueous infrared spectra of IMDA, NTA, and EDTA. Their results are also included in Table II.

<u>Table II</u>

		Observed bands (cm.$^{-1}$)				
<u>Ligand</u>	<u>pH</u>	<u>COOH(A)</u>	<u>COO$^-$(B)</u>	<u>COO$^-$(C)</u>	<u>Predominant Species</u>	<u>Ref.</u>
Iminodiacetic Acid	0.4	1733(s)	-	-	$H_2N^+(CH_2COOH)_2$	13
"	2.2	1721(m)	1619(s)	-	$H_2N^+(CH_2COO^-)(CH_2COOH)$	13
"	4.1	-	1619(vs)	-	$H_2N^+(CH_2COO^-)_2$	13

Table II (Continued)

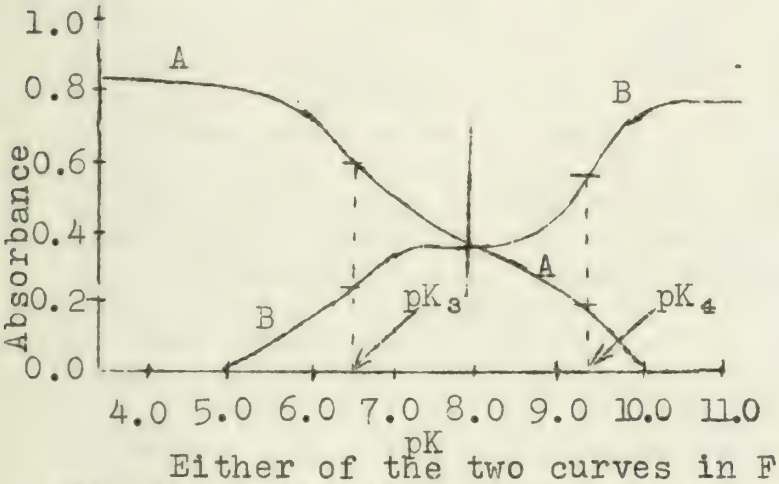
Ligand	pH	Observed bands ($cm.^{-1}$) COOH(A)	COO^-(B)	COO^-(C)	Predominant Species	Ref.
Iminodiacetic Acid	10.9	-	-	1575(vs)	$HN(CH_2COO^-)_2$	13
Nitrilotriacetic Acid	<<1.5	1732	-	-	$HN^+(CH_2COOH)_3$	15
"	<1.5	1730	1635	-	$HN^+(CH_2COOH)_2(CH_2COO^-)$	15
"	2.3	1720(vw)	1623(m)	-	$HN^+(CH_2COOH)(CH_2COO^-)_2$	14
"	5.9	-	1625(vs)	-	$HN^+(CH_2COO^-)_3$	14
"	10.2	-	-	1584(vs)	$N(CH_2COO^-)_3$	14
Ethylenediamine-tetraacetic Acid	<2	~1730	~1635	-	$^-OOCCH_2(HOOCCH_2)N^+H(CH_2)_2N^+H(CH_2COO^-)_2$	15
"	2.7	1700(vw)	1620(s)	-	$^-OOCCH_2(^-OOCCH_2)N^+H(CH_2)_2N^+H(CH_2COOH)(CH_2COO^-)$	16
"	4.0-5.3	-	1625(vs)	-	$^-OOCCH_2(^-OOCCH_2)N^+H(CH_2)_2N^+H(CH_2COO^-)_2$	14,16
"	7.8	-	1624(m)	1585(m)	$^-OOCCH_2(^-OOCCH_2)N(CH_2)_2N^+H(CH_2COO^-)_2$	14,16
"	12.2	-	-	1585(vs)	$^-OOCCH_2(^-OOCCH_2)N(CH_2)_2N(CH_2COO^-)_2$	14

The structural data reported in Table II agree extremely well with results predicted from ionization schemes based upon pK_a data and the known relative acidities of the COOH and R_3NH^+ groups.

Values of pK_a for EDTA were calculated from aqueous infrared data by Martell and coworkers (14). From a plot of the peak intensities of the 1623 cm.$^{-1}$ or 1585 cm.$^{-1}$ carboxylate band against the pH of the solution, the authors were able to obtain approximate pK_a values by taking the pH value at the midpoint of the extreme intensities for each dissociation step. Values of pK_3=6.5 and pK_4=9.3 were obtained from the plot presented in Figure I.

Figure I

Absorbancy of carboxylate bands of EDTA as a function of pH. A, 1623 cm.$^{-1}$ band; B, 1585 cm.$^{-1}$ band.



The intersection of the solid vertical line with curves A and B represents an extreme intensity for each of the two dissociation steps under investigation.

Either of the two curves in Figure I could have been used for the estimation of the pK_a values. The values of pK_3 and pK_4 obtained by this method are in fairly good agreement with those obtained from potentiometric studies (pK_3=6.1, pK_4=10.1).

Aqueous infrared spectroscopy adds another dimension to the study of neutralization reactions of complex molecules. Not only does this technique provide valuable information on solution equilibria (pK_a values), but it also gives information on the structure of the reacting species as well.

(3) Stability and chemical bonding of transition metal ion complexes

The aqueous infrared spectra of several transition-metal ion-amino acid chelates have been obtained by Martell and coworkers (17). From a qualitative study of the variation in the asymmetric and symmetric carboxylate stretching frequencies as a function of metal ion coordination, the authors were able to obtain information regarding the nature of the metal carboxylate link, as well as a relative order of metal-oxygen bond strengths. For a given amino acid in D_2O solution, it was found that the asymmetric carboxylate stretching frequency increased and that the symmetric carboxylate frequency decreased in the following order of metal ions: Ni^{II}-Zn^{II}-Cu^{II}-Co^{III}. This result can best be explained by assuming that the covalent character of the

metal-oxygen bond increases in the order of metal ions given above. Furthermore, since the asymmetric and symmetric carboxylate stretching frequencies shift in opposite directions with a change in metal ion, a chelate structure involving symmetrical coordination of the carboxylate group can be ruled out.

Jones and Penneman (18,19,20) have used infrared spectroscopy in a determination of the successive formation constants of aqueous cyanide complexes of Ag^{I}, Au^{I}, Cu^{I}, Hg^{II}, Cd^{II}, and Zn^{II}. A good discussion of this work was presented in an inorganic seminar given recently by Mr. Khalil (21).

Fronaeus and Larsson (22,23) have investigated a series of metal ion-thiocyanate complexes in aqueous solution by means of infrared spectroscopy. A metal thiocyanate complex in aqueous solution absorbs infrared radiation in the region 2000-2200 cm.$^{-1}$, due to a vibration involving the C≡N stretching mode. For most thiocyanate complexes, this absorption band has a frequency quite distinct from that of the free thiocyanate ion and hence gives unequivocal evidence for the formation of a new molecular species in solution. For some of the complexes studied, it was possible to calculate quantitatively the extinction coefficient and formation constant of the 1:1 species. In addition, a bonding scheme, based upon the variation in frequency and integrated intensity of the complex peak as a function of metal ion coordination was proposed for all of the complexes studied. The work of Fronaeus and Larsson is summarized in Table III.

Table III

Bonding Class	System	ν (cm.$^{-1}$)	ϵ (l/mole cm.$^{-1}$)	$\Delta\nu_{1/2}$	$\epsilon\cdot\Delta\nu_{1/2}\times10^{-4}$	β_1
	SCN^-	2066	537	37	1.99	
I	$Mn^{II}+SCN^-$	2093	655	31	2.03	4.4
I	$Fe^{II}+SCN^-$	2099	-	-	-	-
I	$Co^{II}+SCN^-$	2112	696	29	2.02	8.9
I	$Ni^{II}+SCN^-$	2119	640	32	2.05	15.0
I	$Zn^{II}+SCN^-$	2109	685	34	2.32	8.2
II	$[Co(NCS)_4]^{2-}$	2075	1900	29	4.9	-
II	$Fe^{III}+SCN^-$	2045	1310	49	6.4	-
II	$[Cr(NCS)_6]^{3-}$	2088	937	39	3.7	-
II	$UO_2^{II}+SCN^-$	2066	1100	40	4.4	-
III	$Cd^{II}+SCN^-$	2132	635	24	1.5	-
III	$[Pt(SCN)_6]^{2-}$	2126	246	15	0.4	-
III	$[Hg(SCN)_4]^{2-}$	2112	420	27	1.1	-

ν, frequency of absorption
ϵ, extinction coefficient
$\Delta\nu_{1/2}$, band half width
$\epsilon\cdot\Delta\nu_{1/2}$, approximation to the integrated intensity
β_1, formation constant of 1:1 complex

The class I complexes are considered to be essentially ionic in character with only a very small degree of electron exchange between metal and ligand; they are characterized by an absorption frequency somewhat greater than that of the free thiocyanate ion and an integrated band intensity approximately equal to that of the free thiocyanate ion. The class II complexes are considered to be more covalent in character, with lone-pair donation occurring through the nitrogen end of the ligand; they are characterized by an absorption frequency approximately equal to or less than that of the free thiocyanate ion and an integrated band intensity greater than that of the free thiocyanate ion. The class III complexes are covalent in character, with lone-pair donation occurring through the sulfur end of the ligand; they are characterized by an absorption frequency somewhat greater than that of the free thiocyanate ion and an integrated band intensity somewhat less than that of the free thiocyanate ion.

CONCLUSION

Aqueous infrared spectroscopy is a comparatively new experimental technique. It is a technique which not only provides valuable information regarding the nature of metal-ligand bonding in solution but also is without equal in characterizing the structures of reacting species in aqueous neutralization reactions involving amino acid and amino-polycarboxylic acid molecules. There is no doubt that, in the future, infrared spectroscopy will play an important role in determing the structures of the metal chelates of these molecules in aqueous solution.

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FLASH PHOTOLYSIS AND KINETIC SPECTROSCOPY

Michael R. Rosenthal May 7, 1963

INTRODUCTION AND EXPERIMENTAL (41)

Flash photolysis and kinetic spectroscopy is a powerful method for studying free radicals and transient intermediates in photochemical and thermal reactions. These intermediates, the lifetimes of which are only microseconds or milliseconds, may be photographed in absorption and their rates of growth and decay determined. The fact that they are often produced in vibrationally excited states has led to studies of their relaxation.

A bank of condensers is discharged through a gas, usually xenon, producing a high-intensity flash. Lying parallel and close to the flash tube is a reaction tube. By means of electronic delay circuits, a second flash automatically throws a beam of light through the length of the reaction vessel. The contents are then photographed in absorption by a Littrow spectrograph. A series of such photographs is taken at varying time intervals in order to follow the growth and decay of the species present with time. Plate photometry is used to make these observations quantitative. Representative data for an operation of this type are as follows:

	Photolysis Flash	Spectroscopic Flash
Gas Pressure	10 cm.	10 cm.
Tube Length	50 cm.	10 cm.
Capacity	40 μF.	2 μF.
Voltage	10 Kv.	10 Kv.
Duration	50 μsec.	10 μsec.
Energy	2000 J.	100 J.

The most common studies are kinetic and mechanism studies of explosions (adiabatic) in the gas phase, isothermal gas phase reactions (large excess inert gas), and isothermal flash photolysis of solutions. The spectra obtained are limited to 1900 Å by the transparency limit of quartz, unless special techniques are employed. The outstanding advantage of this method is that unlike conventional photolysis techniques, flash photolysis leads to nearly complete reaction and consequently, high radical or intermediate concentrations.

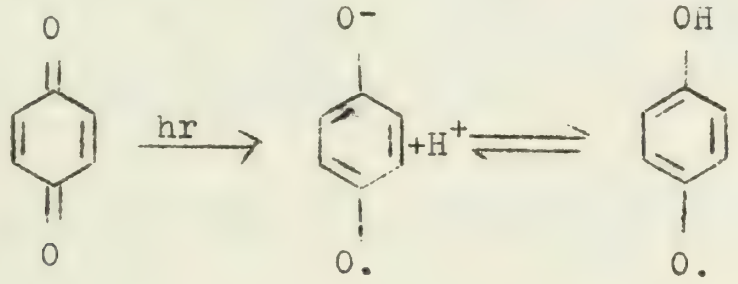
APPLICATIONS

A great deal of work has been done on iodine atom recombination. It was discovered early that the rate of recombination is second order with respect to iodine atoms and first order with respect to a third body (49, 28, 16).

The fact that the rate constant varied for different third bodies was attributed to varying Van der Waals forces in the third body. A reinvestigation, however, indicated that the simple third-order rate law was not obeyed and that the rate constant increased as the ratio of iodine to third body increased (17). This had been previously undetected as a consequence of an opposing thermal effect. New values of the rate constants for several third bodies were obtained by extrapolation. The studies were extended to bromine with argon and oxygen as third bodies (51). The detection of a transient spectrum in the flash photolysis of iodine in benzene (48) led to the proposal that a charge-transfer intermediate was involved. Similar results in other solvents strengthened this proposal (22). A search was undertaken to find such an intermediate in the gas phase (45). A transient spectrum was found when iodine was flash photolyzed in nitric oxide. This was attributed to [NOI] (46). Further work is in progress.

Because of space limitations, the presentation of the other work in this field shall be brief. For more complete information, the reader is referred to the references.

The flash photolysis of quinones has shown the existence of equilibria of the following type: (9, 10).



Rate constants and equilibrium constants have been determined.

The decomposition of carbon dioxide during flash photolysis has been studied and the effect of varying experimental conditions determined (8).

The flash photolyses of nitrosyl chloride, nitrosyl bromide (1,3), and nitric oxide (2,4) have led to the detection of vibrationally excited electronic ground states of nitric oxide.

The adiabatic flash photolysis of sulfur dioxide (37) produced a species identified as a high temperature isomer. Sulfur trioxide was also studied isothermally and mechanisms proposed for its decomposition.

The adiabatic flash photolysis of hydrogen sulfide (36) and the isothermal flash photolysis of carbon disulfide (11) were carried out and mechanisms for their decompositions were postulated.

Several combustion studies of the antiknock properties of tetraethyl lead in hydrocarbons have been made (20,21). The antiknock properties were attributed to the ability of the laed compound to remove oxygenated intermediate species through the formation of lead(II) oxide, which eventually was reduced to elemental lead. Several other hydrocarbon combustion studies have been carried out (34,35) as well as a study of the effectiveness of other additives as antiknock agents (12).

The production of ClO radicals was noted in the flash photolysis of both chlorine-oxygen mixtures (42) and of chlorine monoxide (18). Rate constants were calculated and mechanisms of dissociation and recombination were proposed.

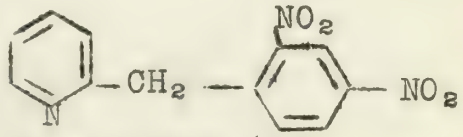
The flash photolyses of aldehydes have been studied under both slow and explosive conditions and mechanisms proposed for their decomposition (24, 32).

The flash photolysis of anthracene-styrene mixtures was found to lead to polymerization of the styrene through the formation of the triplet state of anthracene (38). The triplet state of anthracene in hexane solution has been studied in great deail (43). The flash photolysis of mercury vapor has led to formation of the triplet state (15). The subject of radiationless transitions from triplet to singlet states has been discussed in detail (44).

Nickel tetracarbonyl was flash photolyzed under isothermal conditions in several gases and a mechanism for its decomposition was proposed (13,14).

The flash photolyses of ammonia (23), deuterated ammonia (23), phosphine (27,28), and deuterated phosphine (27,28) led to detection of NH_2, ND_2, PH_2, and PD_2 radicals, respectively, and to postulation of mechanisms of formation and decay. The flash photolysis of phosphine in oxygen was also studied (40).

The color change of the substance



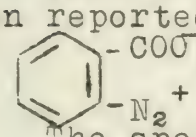
in water was studied by means of flash photolysis (53).

The isothermal flash photolysis of azomethane (50) and hydrogen azide (52) have been carried out. Intermediates and decomposition mechanisms have been postulated.

Flash photolysis has been used to study and characterize methyl and methylene radicals (25) and to determine acidity constants for several organic molecules in their lowest triplet states (26).

Flash photolysis has been used to study ozone decomposition (29,31) and the formation of vibrationally excited oxygen from the isothermal decomposition of chlorine dioxide and nitrogen dioxide(27).

Vibrationally excited CN radicals have been produced in the flash photolyses of cyanogen, cyanogen bromide, and cyanogen iodide (5).

The first observation of the spectrum of benzyne has been reported as a transient spectrum in the flash photolysis of 

(6).
The spectral range has been extended to 1500 Å in a flash photolysis of water vapor (7).

A flash photolysis study of inorganic halides in solution has produced transient spectra associated with dihalide anions(19).

Flash photolysis has been used to study the combustion of methyl iodide in great detail (33).

The mechanism of relaxation of vibrationally excited states produced in flash photolyses and the energy distribution among them have been discussed (30).

CONCLUSION

The formation of short-lived intermediates and free radicals in concentrations higher than those produced by more conventional methods has prompted studies elucidating fast-reaction kinetics and mechanism. The growing interest in this area promises much more useful data and an interesting future for the study of "instantaneous" reactions.

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THE MÖSSBAUER EFFECT AND ITS APPLICATIONS TO INORGANIC CHEMISTRY

K. F. Purcell May 14, 1963

INTRODUCTION

Nuclear resonance spectroscopy is a spectroscopic method that possesses several unique features. As the name implies, nuclear resonance absorption is the resonant excitation of nuclei. Very briefly, the experimental procedure requires a source of the resonant γ-energy mounted on a variable velocity mechanism, an absorber (sample), and a detector. The intensity of γ-rays passing through the absorber is plotted as a function of the source velocity. The resulting spectrum will yield information about the electron density at the nucleus and molecular symmetry.

THEORY

Consideration of a particle which emits a photon shows that there is a recoil momentum associated with the emission(1). For low energy photons, the recoil is negligible, but in the present situation where $E_\gamma \approx 10\text{-}100$ k ev., the recoil energy loss can be appreciable ($\approx 10^{-2}$ ev.). It is given by $R = \frac{E_\gamma^{\,2}}{2\,mc^2}$. For emitting (absorbing) nuclei tightly bound in a crystal of "finite" size, the crystal absorbs the recoil and because of the large mass of the crystal the recoil velocity and energy transferred to the lattice are negligible. There is another mechanism for recoil energy loss to the lattice, however. Emission of a γ-ray may cause excitation of lattice vibrational modes and lead to a loss of energy (1,2,3,4). Any emission event which occurs leaving the lattice in its initial vibrational state is termed "recoilless". Recoilless resonance is also called Mössbauer resonance, after the man who discovered it (5).

We shall now consider the crystal properties and experimental conditions which lead to Mössbauer resonance (1,4). A real crystal is assumed to possess the properties of a Debye solid. For such a substance, Debye showed that the distribution of vibrational frequencies is proportional to frequency squared, as indicated in Figure 1.

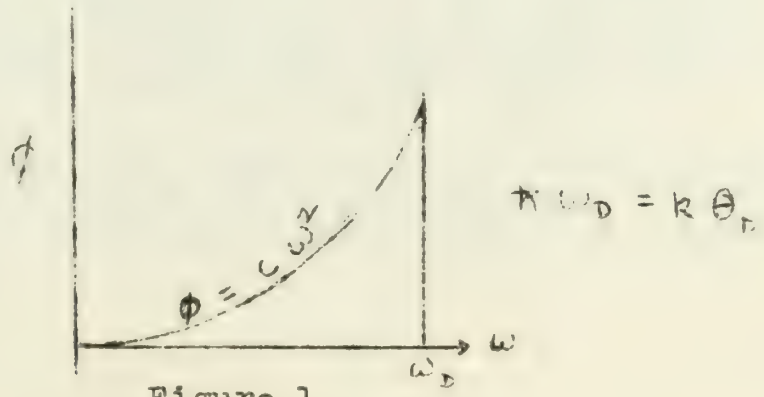

Figure 1

There are no vibrations with $\underline{W} > \underline{W}_D$, the "cut-off" frequency. As far as we are concerned, this relationship means that there are more high-energy modes than low. Quantum theory tells us that the average energy transferred to the lattice for an emission event is

$$\bar{\underline{R}} = \sum_f \underline{P}(f \leftarrow i) \quad (\underline{E}_f - \underline{E}_i) = \underline{E}_\gamma^2/2\underline{MC}^2$$

where $\underline{E}_i$ and $\underline{E}_f$ are the initial and final lattice energies and $P(f \leftarrow i)$ is the probability for the lattice going from state $\underline{i}$ to state $\underline{f}$ during emission. If we assume that the Debye model applies, the Mössbauer effect will be greatest when the crystal possesses a high Debye temperature and when the temperature of the crystal is low.

The fact that $\bar{\underline{R}} = \underline{E}_\gamma^2/2\underline{MC}^2$ restricts the occurrence of the Mössbauer effect to nuclear transitions for which $\underline{E} < 150$ kev. (assuming a <u>maximum</u> realistic θ_D). The dependence of the Mössbauer effect on $\underline{E}$, $\underline{\theta}_D$, and $\underline{T}$ is shown in Figure 2 (2).

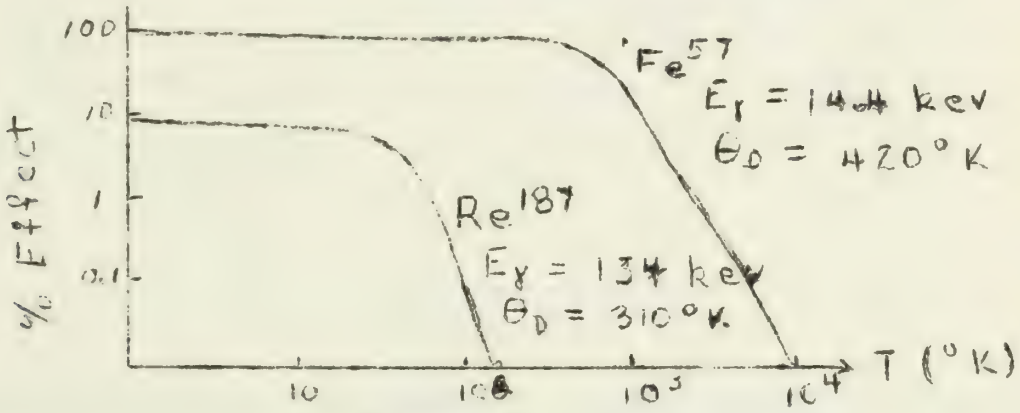

Figure 2

Two aspects of chemical structure - electron distribution and molecular symmetry - play a significant role in determining the nature of the Mössbauer spectrum of a molecule. Molecular symmetry is reflected in the spectrum of a nucleus which possesses a quadrupole moment, through the presence (or lack) of a quadrupole split resonance line (6). The effect of a difference in electron densities at source and absorber nuclei is termed "isomer shift", and such a difference determines the position of the resonance line in the spectrum(1). This is because the nuclear energy levels are shifted slightly by a change in electrostatic interaction with the extranuclear electrons. Since "s" electrons have the greatest density at the nucleus, changes in "s" wave functions at the nucleus are of most importance in producing the isomer shift.

In the case of the iron compounds to be discussed later, increasing "s" density over a series of compounds produces a progressively smaller isomer shift with respect to a given

source (7,8). The nuclide Fe^{57} also possesses a quadrupole moment in the excited state but not in the ground state (6).

EXPERIMENTAL PROCEDURE

In order to "match" the energy of the emitted γ ray to that required for absorption, the frequency is shifted by the linear Doppler effect (1). The source (usually) is placed on a velocity drive and driven toward or away from the absorber with a known velocity. The intensity of γ rays passing through the absorber is measured by a NaI(Tl) scintillation counter and plotted as a function of the velocity. Mössbauer used a record turntable as a velocity mechanism (5). The apparatus most commonly used now is shown schematically in Figure 3 (1).

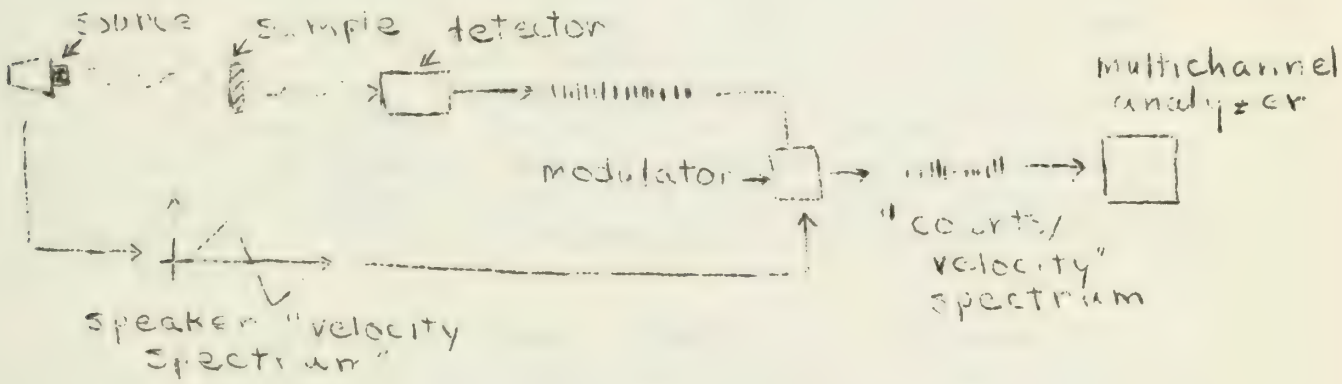

Figure 3

The source, mounted on the speaker, is driven with changing velocity as shown in the "velocity spectrum". The counting pulses from the detector are modulated with this velocity spectrum, and a multichannel analyzer sorts the pulses as a function of velocity.

Mössbauer resonance has been observed for 16 nuclei, all of interest to the inorganic chemist(1). These nuclei are Fe^{57}, Ni^{61}, Zn^{67}, Sn^{119}, Gd^{155}, Dy^{161}, Er^{166}, Tm^{169}, Yb^{170}, Hf^{177}, Ta^{181}, W^{182}, Re^{187}, Ir^{191}, Ir^{193}, and Au^{197}.
To illustrate source and absorber preparation, the procedure for Fe^{57} experiments will be outlined. The nuclide Co^{57} undergoes electron-capture decay to excited state Fe^{57}, which falls to the ground state emitting the 14.4 kev. γ ray (1,3). The Co^{57} nuclide, then, is the source for Fe^{57} Mössbauer experiments. The standard "iron" source is prepared by depositing Co^{57} on a thin sheet of 310 stainless steel and heating to diffuse the cobalt into the steel (9). This source emits a monoenergetic γ ray. The sample, the spectrum of which is desired, may be a very thin crystal, a small amount of powder (10), or a thin layer of "frozen" liquid (11).

An important correction to the isomer shift must be made when one wishes to compare the results of experiments performed at different temperatures. The correction is for the "second-order Doppler effect" and arises as a result of the temperature dependence of the lattice particle kinetic energy. The "temperature shift" has been shown to be given by

$$\frac{\Delta v}{\Delta T} = -2.4 \times 10^{-15}\, v\,(^{\circ}K)^{-1}$$

where v is source velocity at resonance (12,13).

CHEMICAL APPLICATIONS

One of the earliest papers in which an attempt was made to correlate the isomer shift (δ) and quadrupole splitting (ΔE) with molecular properties is that of Ingalls and coworkers(7). Their results (see Table) indicate that "ionic" Fe(II) has a $\delta \approx 1.0$-1.5 mm. sec.$^{-1}$ and "ionic" Fe(III) $0.40 < \delta < 1.0$ mm. mm. sec.$^{-1}$. It is seen that ΔE for Fe(III) is zero except for Fe_2O_3, whereas ΔE for the Fe(II) salts ranges from 1.80 mm. sec.$^{-1}$ to 3.20 mm. sec.$^{-1}$. These authors explained the effect of the oxidation state of iron on the quadrupole splitting as due directly to asymmetry of charge distribution in the 3d shell.

Their argument breaks down, however, in the case of Fe $Fe(CN)_6$. In view of the data available it is more logical to consider ligand-field distortions as giving rise to the splittings. Such distortions may be transmitted to the nucleus through the 3p electrons and/or by asymmetric shielding of the "s" electrons by the "d" electrons (14). Although these "mechanisms" are useful in correlating the data there have been no calculations to support them. The large ΔE found for the Fe(II) salts is believed to be due to tetragonal and rhombic distortions of the octahedral field about the nucleus. X-ray investigations(16) have shown this to be the case for $Fe(NH_4)_2(SO_4)_2.6H_2O$.

Several workers (10,14) have reported Mössbauer resonance data for the simple and complex iron cyanides, and Epstein (10) has reported spectra for a number of "ionic" and "covalent" iron complexes. The isomer shifts for all of the iron cyanides indicate extensive Fe $\rightarrow$ CN^- π bonding and close approach of the ligands to the iron ion in the anions. The quadrupole splittings may be rationalized by considering the electronic configuration about the iron nuclei and the effects of crystal distortions. In the mixed complex cyanides, the spectra indicate that Fe(II) resides in the carbon hole(15). The ΔE of 0.4 mm. sec.$^{-1}$ for Fe(III) in $KFe_2(CN)_6$ is attributed to lattice water of crystallization. A similar proposal applies to $Na_3Fe(CN)_6 \cdot H_2O$. The spectrum of sodium nitroprusside, $Na_2Fe(CN)_5NO \cdot 2H_2O$, has been interpreted (10) as indicating iron in an oxidation state of +4.

Table I

Compound	ΔE (mm.sec.$^{-1}$)	δ (mm.sec.$^{-1}$)	Reference
Fe_2O_3	0.24±0.03	0.47±.03	7
$Fe_2(SO_4)_3$	0.0	0.55±.05	7
$FeCl_3$	0.0	0.45±.05	7
$FeCl_2 \cdot 4H_2O$	3.00±.05	1.35±.05	7
$FeSO_4 \cdot 7H_2O$	3.20±.05	1.40±.05	7
$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	1.75±.05	1.40±.05	7
FeF_2	2.68	1.40±.05	7
$K_3Fe(CN)_6$	0.26±.05	-0.10±.05	10, 14
$K_4Fe(CN)_6 \cdot 3H_2O$	0.0	0.0±0.05	14, 10
$Na_3Fe(CN)_6 \cdot H_2O$	0.60	-0.05	10
$Na_2Fe(CN)_5NO \cdot 2H_2O$	1.76±0.01	-0.17±0.01	10
$Fe_4[Fe(CN)_6]_3$	-0.02 +0.55	0.0 (anion) 0.0 (cation	10
$Fe_2(CN)_6$	0	0.0±0.1 (Anion)	
	0	0.53±0.1 (Cation)	14
$KFeFe(CN)_6$	0	0.0±0.1 (Anion)	
	0.4±0.05	0.53±0.05 (Cation)	14
$K_2FeFe(CN)_6$	0.6±0.2	0.3±0.2 (Anion)	
	1.8±0.2	0.93±0.2 (Cation)	14

Epstein(10) and Wertheim and coworkers(11) have shown that Mössbauer resonance can be obtained from molecular crystals (e.g., Fe(II) Phthalocyanine, $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$). There has been a prodigous amount of infrared, x-ray, and kinetic data published on the structure of $Fe_3(CO)_{12}$ (11). The Mössbauer spectrum of the compound shows the molecule to have the 3,3,3,3 structure in agreement with the kinetic studies and one interpretation of the infrared spectrum.

CONCLUSION

In view of the complex molecules to which Mössbauer resonance has been applied, it is not surprising that ambiguities exist in interpreting their spectra. It is necessary that a detailed systematic selection of compounds be made to examine the effects of σ and π bonding and ligand-field symmetry on the spectra.

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HYDROLYSIS OF METAL IONS

J. E. House, Jr. May 23, 1963

INTRODUCTION

The aqueous solutions of most heavy metal ions are acidic. In the process of solution, some reaction takes place in which protons are liberated producing solutions which are acidic. Historically, the process has been written as

$$M^{Z+} + zH_2O \rightleftarrows M(OH)_z + zH^+ \quad . \tag{1}$$

Since this requires the solid metal hydroxide to be present or a solution of the hydroxide, neither of which is observed in many systems, this is not a very accurate representation. Others are

$$M(H_2O)_n^{z+} + H_2O \rightleftarrows M(H_2O)_{n-1}OH^{(z-1)^+} + H_3O^+ \tag{2}$$

and

$$M^{z+} + H_2O \rightleftarrows M(OH)^{(z-1)+} + H^+ \quad . \tag{3}$$

Since many ions (e.g. Be^{2+}, Fe^{3+}, UO_2^{2+}, Bi^{3+}, etc.) produce acidic solutions, these reactions are fairly general. It is now known that fairly complicated hydrolysis products are produced in which two or perhaps even several metal ions form polynuclear species. Since the number of ions which hydrolyze to give acidic solutions is fairly large and several studies have been made on most of them, no attempt is made here to give a complete survey of the literature of hydrolytic processes. For a more complete survey of the literature, one should consult the Tables of Stability Constants (1). Neither are anionic hydrolysis reactions considered here.

THEORY AND TREATMENT OF DATA

To present an outline of the general methods used to describe hydrolytic equilibria, use will be made of the following:

List of Symbols

A = the ligand species
B = the central metal ion
C_B = total concentration of species B
C_A = total concentration of species A
$\bar{n}$ = the average number of ligands bound to B
a = the concentration of free (unbound) A
b = the concentration of free (unbound) B
h = the concentration of H^+ set free by hydrolysis
K_w = the ion product of water
β_{qp} = the formation constant of complex $[B_qA_p]$, $[B_qA_p]/ab$
χ_{qp} = the hydrolysis constant

For the hydrolysis of metal ions

$$qB + pH_2O \rightleftarrows Bq(OH)_p + pH \qquad (4)$$

where the ionic charges have been omitted. The hydrolysis constants χ_{qp} are given by

$$\chi_{qp} = \frac{[Bq(CH)p]h^p}{b^q} = \beta_{qp}K_W^p \qquad (5)$$

where the β_{qp} is the formation constant of the complex formed by the reaction

$$qB + pOH \rightleftarrows Bq(OH)p \qquad (6)$$

and is given by

$$\beta_{qp} = \frac{[Bq(OH)p]}{[B]^q[OH]^p} \quad . \qquad (7)$$

The problem of determining the extent of hydrolysis as occurring in equation (5) and the hydrolysis constants is intimately related to the stability of the hydroxo complexes formed. In order to discuss the extent of hydrolysis, the determination of stability constants must be considered. A brief survey of the methods used in the treatment of data will be given. The methods used for mononuclear complexes will be considered first.

MONONUCLEAR COMPLEXES

A. Bjerrum's Method (2).

The average number of ligands attached to the central metal ion B is given by

$$\bar{n} = \frac{C_A - a}{C_B} = \frac{\sum_{i=1}^{p} i[BA_i]}{b + \sum_{i=1}^{p} [BA_i]} \quad . \qquad (8)$$

By making use of the definition of the formation constants

$$\bar{n} = \frac{\beta_1 a + 2\beta_2 a^2 + --- + p\beta_p a^p}{1 + \beta_1 a + --- + \beta_p a^p} \quad . \qquad (9)$$

This can be written as

$$\bar{n} = (\bar{n} - 1)\beta_1 a + (\bar{n} - 2)\beta_2 a^2 + --- + (\bar{n} - p)\beta_p a^p = 0 \qquad (10)$$

The values of the β's where p experiments have been performed giving p equations (8) are obtained by solution of the p equations using determinants.

The expression (6) cannot be used to determine $\bar{n}$ when weak complexes are formed or where the central ion is present in very small concentrations because under these conditions $C_A \simeq a$. In this case, the degree of formation of the complex, α_p, is used.

$$\alpha_p = \frac{[BA_p]}{C_B} = \frac{\beta_p a^p}{1 + \sum_{i=1}^{p} \beta_i a^i} \qquad (11)$$

Using equation (9) and the definition of $\bar{n}$, it is possible to derive the expression for $\bar{n}$,

$$\bar{n} = p - \frac{\partial \ln \alpha_p}{\partial \ln a} \qquad (12)$$

If the concentration of the central ion or any one of the complexes is known as a function of the free ligand concentration, it is possible to obtain $\bar{n}$ by graphical differentiation of the curve one gets from plotting log a against log α_p. The plot of $\bar{n}$ against log a gives the formation curve of the system. Where the measured quantity is the free metal ion concentration, b,

$$\bar{n} = \frac{\partial \log b}{\partial \log a} \qquad (13)$$

Again $\bar{n}$ can be determined for the system but here the approximation $C_A \simeq a$ is not valid since the experimentally determined quantity is not "a" itself. The graphical method of successive approximation must be used to find $\bar{n}$ and a. From equations (7) and (9), α_c and $\bar{n}$ are functions of "a" only for mononuclear complexes.

This method applies to all systems whether the measured quantity be the concentration b, a, or one of the complexes BA_p. A plot of $\bar{n}$ against a, the free metal ion concentration, immediately indicates the number of complexes which must be dealt with.

B. Leden's Method (3)

A function of the concentration of free A, F(a), is defined by

$$F(a) = \frac{C_A - a}{ba} = \sum_{i=1}^{p} \beta_p a^{p-1} = \beta_1 + \beta_2 a + \text{---} + \beta_p a^{p-1} \qquad (14)$$

From a plot of $F(a) = \frac{C_A - a}{ab}$ against a, the limit

$$\lim_{a \to o} F(a) = \beta_1$$

is obtained graphically. The successive constants may be obtained

from other functions G(a) where

$$G(a) = \frac{F(a) - \beta_1}{a} = \beta_1 + --- + \beta_p a^{p-2} \quad . \tag{15}$$

The graphical limit is determined again for G(a) and yields β_2 since

$$\lim_{a \to o} G(a) = \beta_2 \tag{16}$$

As an alternate to this method of extrapolation, the values of the β's may be determined by solving a system of linear equations by means of determinants.

Fronaeus (4) has developed a similar method which uses the concept of $\bar{n}$ along with a limiting process of evaluation of the formation constants. This method can be shown to be equivalent to the Leden method by a simple transformation of the F(a) function of Leden to the function defined in Fronaeus' method. A complete review of these methods and typical calculations involving their use has been given by Sullivan and Hindman (5).

A large number of graphical and empirical methods have been developed which are less general in scope (6-14).

Methods involving the use of digital computers have also been devised for the solution of the linear equations for the values of the stability constants (15,16).

POLYNUCLEAR COMPLEXES

Most metal ions produce polynuclear complexes on hydrolysis. The theory of such processes has been worked out in great detail and the description of some of the more general methods specifically treating hydrolytic processes follows (17,19).

The total concentration of the central ion and ligand are given by

$$C_B = \sum_{q=1}^{Q} \sum_{p=o}^{P} q\,[B_q A_p] = \sum_{q=1}^{Q} \sum_{p=o}^{P} q\,\beta_{qp} b^q a^p \tag{17}$$

$$C_A = a + \sum_{q=1}^{Q} \sum_{p=1}^{P} P[B_q A_p] = a + \sum_{q=1}^{Q} \sum_{p=1}^{P} P\beta_{qp}\, a^p b^q \tag{18}$$

where P and Q are the maximum values of p and q found in complexes of B and A respectively. The total concentrations of A and B are known either from amounts of materials used to make up the starting solutions or from analytical information. The formation constants β_{qp} of equations (17) and (18) can be determined if a and b can be determined. From equations (17) and (18) the average number of ligands bound per metal ion is

$$\bar{n} = \frac{C_A - a}{C_B} = \frac{\sum_{q=1}^{Q} \sum_{p=1}^{P} p\beta_{qp}\, b^q a^p}{\sum_{q=1}^{Q} \sum_{p=o}^{P} q\beta_{qp}\, b^q a^p} \quad . \qquad (19)$$

The ratio of total metal ion concentration to free (unhydrolyzed) metal ion concentration is

$$F_o = \frac{C_B}{b} = \sum_{q=1}^{Q} \sum_{p=o}^{P} q\, \beta_{qp}\, b^{q-1} a^p \quad . \qquad (20)$$

For polynuclear complexes, $\bar{n}$ and F_o are functions of ligand concentration, a, and free metal ion concentration, b. The quantities $\bar{n}$ (a) and F_o (a) can be calculated using (19) and (20) for a series of values of C_B for those systems in which corresponding values of C_A, C_B, a, and b may be measured.

A. The Method of Jensen (17).

The equation for $\bar{n}$ is considered where concentration ranges are such that only two complexes can exist at the same time; B_qA_y and B_rA_x, where B_rA_x is thought of as the product in a reaction of B_qA_y with B and A so that $x/r > y/q$ or the ratio A to B has increased. From this and the defining equation for $\bar{n}$ is derived

$$\frac{\bar{n}}{\frac{x}{r} - \bar{n}} = \frac{r[B_rA_x]}{q[B_qA_y]} \quad . \qquad (21)$$

Two limiting cases are considered for this simplified relationship for $\bar{n}$. The first is for $x/r \gg \bar{n}$. For this case, the relationships

$$\left(\frac{\partial \log C_B}{\partial \log a}\right)_{\bar{n}} = \frac{qx-ry}{q-r} = \frac{X - \frac{r}{q}y}{1 - \frac{r}{q}} = t \qquad (22)$$

and

$$\left(\frac{\partial \log \bar{n}}{\partial \log a}\right)_{C_B} = \frac{qx-ry}{q} = X - \frac{r}{q}y = m \qquad (23)$$

are derived. This condition is equivalent to a case where a complex B_rA_x dominates the expression for the concentration of A bound in complexes with B and at the same time a complex B_qA_y dominates the expression for C_B. A plot of log $\bar{n}$ vs log C_B or a plot of log $\bar{n}$ vs

log a is linear. The values of m and t may be determined from the slopes of the experimental curves. From the two equations thus obtained, only two independent ratios among the four variables r, q, x, and y can be determined.

The second case applies for the condition $x'/r' \simeq n$. For this case, similar equations are derived and define slopes m' and t'.

The equations define an infinite number of sets of values (r,x), (q,y), (r',x'), and (q',y'). Independent data are needed to choose proper values although the ratios are determined. The advantage of this method is that, in many cases, the primary hydrolysis product can be determined with certainty.

B. Core-Links Treatment (18,19,20)

Sillén (18) has shown that a large number of complexes produced on hydrolysis may be considered to be made up of a central group, the core, held to a number of composite groups, the links, containing the central group. These are represented as $B_s(A_tB)_m$. These polynuclear complexes give parallel curves for plots of $\bar{n}$ vs $(\log a)_{C_B}$ or $\log F_o$ vs $(\log a)_{C_B}$. The spacings between the curves can be shown to be

$$t = -\left(\frac{\log C_B}{\log a}\right)\bar{n} \quad . \tag{24}$$

From the definitions of C_B and C_A, the function $\log(C_B/b)$ is

$$\log C_B b^{-1} = \log\left[1 + \sum qa^p b^{q-1}\beta_{qp}\right] \quad . \tag{25}$$

The total concentrations of A and B are known, as described in the discussion of mononuclear complexes and a and b are measured as C_B is held constant while varying C_A within the maximum limits possible without precipitation of metal hydroxide. Sillén (18) has shown that if the plots of $\bar{n}$ vs log a with C_B held constant are parallel and the amount of free B is not negligible compared to C_B, all the complexes present in appreciable amounts must have the general formula $B(A_tB)_m$ where t is given by equation (24). It has also been shown that if the curves from a plot of $\log(C_B/b)$ vs log a at constant C_B are parallel, the formula for the complexes must be $B(A_tB)_m$ with t constant and m variable. If the curves also coincide, only mononuclear complexes are present since the extent of hydrolysis would be a function of "a" only in this instance.

C. Hedström's Method (21)

In this method, no assumption whatsoever is made regarding the nature of the complexes formed. By elimination of p, q, and β_{pq}, the general relationship is obtained as

$$\left(\frac{\partial C_B}{\partial \ln a}\right)_b = \left(\frac{\partial C_A}{\partial \ln b}\right)_a \quad . \tag{26}$$

This applies to one or more of the B_qA_p complexes formed. This equation is subject to the boundary conditions $\ln(a/C_A) = 0$ at $C_B = 0$ and $\ln(b/C_B) = 0$ at $C_A = 0$. Solving equation (26) for $\log(a/C_A)$ leads to

$$\log(a/C_A) = \left[\int_0^{C_B} \left(\frac{\partial \log(b/C_B)}{\partial C_A}\right)_{C_B} dC_B\right]_{C_A} . \quad (27)$$

Similarly

$$\log(b/C_B) = \left[\int_0^{C_A} \left(\frac{\partial \log(a/C_A)}{\partial C_B}\right)_{C_A} dC_A\right]_{C_B} . \quad (28)$$

For each series of experiments at constant C_B, one plots $\log(b/C_B)$ against C_A and determines the derivative of these curves at certain C_A values. The corresponding value of the $\log(a/C_A)$ is obtained from the area under the curve obtained when $\left(\frac{\log b/C_B}{C_A}\right)_{C_B}$ is plotted against C_B. A similar operation is used for the second equation. This method necessitates measurement at a large number of different values of C_B (or C_A if the other equation is used). A wide range of concentrations should be used.

The evaluation of formation constants is accomplished by use of

$$F_1 = \frac{C_B - b}{a\,b} = \sum_{p,q} \beta_{pq}\, a^{p-1} b^{q} . \quad (29)$$

When $q = 1$, F_1 is a function of "a" only, which means the complexes are mononuclear and the problem is the same as formulated by Leden for the mononuclear case. To evaluate the degree (maximum q) of the polynuclear process, a plot of F_1 vs b at certain constant values of a is made. If a straight line results, only mononuclear and dinuclear complexes are present. If a parabola results, trinuclear complexes are present, etc. From the plot of F_1 vs b, the intercept $I_1 = \sum_p \beta_{p1} a^{p-1}$ is obtained.

Now let

$$F_2 = \frac{F_1 - I_1}{ab} \quad (30)$$

be plotted against b. The next intercept $I_2 = \sum_p \beta_{p2} a^{p-2}$ is obtained. This process is repeated until a straight line is obtained. For each value of p, q can have more than one value. In order to find all the formation constants, the F curves obtained at different constant values of a are compared. The resulting system of equations will enable calculation of the β_{qp}'s. This method will be illustrated for a specific case.

TYPICAL HYDROLYTIC PROCESSES

A. Hg^{2+}

The hydrolysis of Hg^{2+} has been studied by measuring the solubility of HgO in water (22) at 25°. From the value of the solubility product of $Hg(OH)_2$ (using the value of $pK_w = 14$), the sum $pKa_1 + pKa_2$ was calculated to be 6.26.

A more recent and much more thorough study was made by Hietanen and Sillén (23) using emf measurements. The process was found to be one in which $\bar{n}$ is a function of log h only and independent of C_B. From the discussion of the treatment of data, this was seen to be the criterion for the formation of mononuclear complexes only. An analysis of the data by the methods described shows the main products of the hydrolysis to be $Hg(OH)_2$ and $HgOH^+$ corresponding to the reactions

$$Hg^{2+} + H_2O \rightleftarrows HgOH^+ + H^+;\ pKa_1 = 3.70 \pm .07$$

$$Hg^{2+} + 2H_2O \rightleftarrows Hg(OH)_2 + 2H^+;\ pKa_2 = 2.60 \pm .09 \quad .$$

The k's are the first and second acid constants of the acid $Hg(H_2O)_n^{2+}$.

B. Fe^{3+}

The hydrolysis of Fe^{3+} has been studied for many years by a variety of techniques and a variety of results have been obtained (24,26. See references 1 and 26 for complete references to the earlier literature). Hedstrom (26) has studied the hydrolysis of Fe^{3+} using emf measurements. The free hydrogen ion concentrations were determined by a glass electrode, and the concentration of Fe^{3+} from the half cell $|Fe^{3+}, Fe^{2+}|$ Pt. The reference electrode used was a calomel electrode,

$$|\ Hg,\ Hg_2Cl_2\ |\ 4\ \underline{M}\ NaCl\ |\ 3\ \underline{M}\ NaClO_4|\ .$$

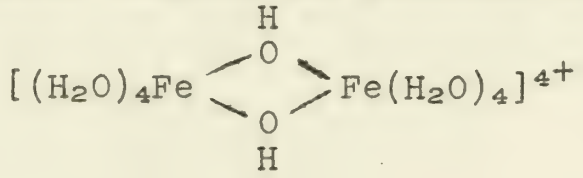
The hydrolysis of Fe^{2+} has been shown to be negligible in solutions of pH < 5 (27). The following species were identified from an analysis of the data.

$$Fe^{3+} + H_2O \rightleftarrows Fe(OH)^{2+} + H^+;\ \log \beta = -3.05$$

$$FeOH^{2+} + H_2O \rightleftarrows Fe(OH)_2^+ + H^+;\ \log \beta = -3.26$$

$$2Fe^{3+} + 2H_2O \rightleftarrows Fe_2(OH)_2^{4+} + 2H^+;\ \log \beta = -2.91 \quad .$$

The predominant species present is the dinuclear complex with the two mononuclear species becoming more important at low total concentrations of Fe(III). The dinuclear complex was presumed to be



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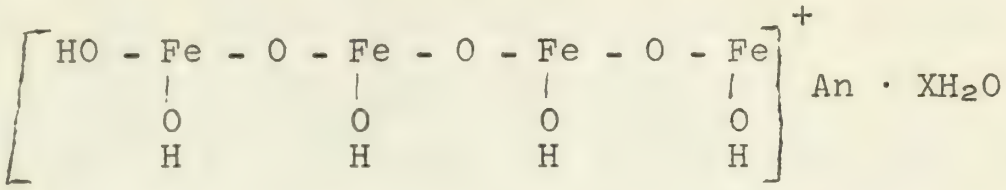
In the conductometric titration of Fe^{3+} with base (25), the first inflection point could not be attributed to the formation of $Fe(OH)_3$ but rather some intermediate complex. This intermediate was separated and the composition found to be $[Fe_4O_3(OH)_5]NO_3 \cdot 4H_2O$. The structure suggested was



where An represents a univalent anion. This structure is reported to be similar to some of the α-series minerals of iron.

The hydrolysis products $Fe(H_2O)_6^{3+}$, $Fe(H_2O)_5OH^{2+}$, $Fe(H_2O)_8(OH)_2^{4+}$, and $Fe(H_2O)_4(OH)_2^{+}$ have also been reported on the basis of similar base additions (24).

C. Bi^{3+}

The hydrolysis of Bi^{3+} has been studied by Olin (28,29) using a glass electrode to determine the free concentration of H^+ and a bismuth amalgam electrode to measure the Bi^{3+} concentration. The first step in the hydrolysis leads to $Bi_6(OH)_{12}^{6+}$. In solutions of lower pH, this forms larger aggregates. The data can be interpreted in terms of the formation of $Bi_9(OH)_{20}^{7+}$, $Bi_9(OH)_{21}^{6+}$, and $Bi_9(OH)_{22}^{5+}$ as the polynuclear species present in the aggregate.

Previously, Graner and Sillén (30) had interpreted the data obtained from similar experiments in terms of the formation of $Bi[(OH)_2Bi]_n^{(3+n)+}$ written in core-links form. The identity of this product was determined by studying a concentration range of Bi^{3+} from 10 to 50 mM. The study of Olin (28) was made over a range of 0.1 to 50 mM. The quinhydrone electrode was used to measure the concentration of H^+ and was later found to have appreciable basicity at the concentrations of H^+ used (31). The formula for this product would be written as $Bi_{n+1}(OH)_n^{(3+n)+}$ in conventional form and is seen not to be the product found by Olin. This is a typical example of the difficulties encountered and the conclusions drawn in the study of such systems.

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MOLECULAR ORBITAL TREATMENT OF POLYHALOGEN AND RELATED SPECIES

Carolyn M. McArthur May 28, 1963

INTRODUCTION

The halogens interact to form a wide variety of species besides the familiar halogen diatomic molecules X_2. These can be classified as the inter-halogen compounds XY, XY_3 (T-shaped, C_{2v}), XY_5 (square pyramidal, C_{4v}), XY_7 (pentagonal bipyramidal, D_{5h}); the polyhalide ions X_3^- (linear), I_n^- [(n odd), e.g., I_5^- (V-shaped, C_{2v})], I_8^{2-} (chair shape, C_{2h}), XY_2^- and XYZ^- (both linear), XY_4^- (square planar, D_{4h}); and the positive polyhalogen ions XY_2^+ (angular, C_{2v}) and XY_4^+ (structure unknown).

Many of these polyhalogen species, if described in valence bond terms, violate the Lewis octet rule of valency theory (1) with over-filled electron shells. The common solution has been to use an outer d-orbital to provide the necessary extra orbital(s), but this d-orbital does not belong to the valence orbitals. Nevertheless, hybrid valence structures using outer d-orbitals have been postulated, with lone pairs of electrons assumed to occupy one or more of the hybrid orbitals. Explanations involving electron-pair repulsions have been invoked to correlate the possible structures predicted by hybridization considerations with the actual shape of molecules like T-shaped ClF_3. (See, for example, Gillespie and Nyholm (2).) However, even Pauling (3) has sometimes been cautious in describing structures in terms of outer d-orbitals, noting that resonating Lewis electronic structures probably make a considerable contribution to the electronic ground state of such molecules.

The placing of lone pairs of electrons in high energy hybrid orbitals is a significant objection to the valence bond description using outer d-orbitals. Only in IF_7 are all the valence shell electrons of iodine involved in bonding. Inherent in this description is the assumption of easy orbital excitation from a p to a d level when the principal quantum number remains unchanged, but this assumption has no basis in experimental fact. For example, it is often assumed that compounds of F and Cl differ in structural properties because of d-hybridization in chlorine. In fluorine, the energy of the center of gravity of states arising from $2s^2 2p^4(^3P)3d$ is 15.9 e.v. (4); that arising from $3s^2 3p^4(^3P)3d$ is 11.2 e.v. (5,6). In both F and Cl the excitation energy is large, in each case being only slightly less than 2 e.v. below the ionization limit, and Klemperer (7) points out that it is extremely arbitrary to single out the configuration of Cl involving a 3d electron from the wealth of configurations near the ionization limit. The selection of a single excited configuration as predominant is only useful if this configuration lies uniquely lower in energy than others.

A striking structural feature of these compounds is that, with the exception of IF_7, the bond angles are all very close to 90° or 180°. In 1951, Pimentel proposed a bonding scheme for trihalide ions based on molecular orbitals formed from linear combinations of np_σ halogen orbitals, which excludes the need for higher energy orbitals (8). Hach and Rundle (9) independently proposed the same type of MO scheme, but applied it only to the polyiodides. Havinga and Wiebenga have extended the LCAO-MO method to all the polyhalogen species and have obtained a consistent qualitative explanation of bond angles, atomic configurations, and bond lengths (10, 11).

MO BONDING SCHEME FOR POLYHALOGENS

In the modified Hückel LCAO-MO treatment used by Wiebenga and co-workers, only atomic p-orbitals of the halogens are considered. Overlap integrals are neglected, and all resonance integrals are taken as zero, except those involving orbitals of neighboring atoms in the bond direction, which are given the same value β (Hückel approximations (12)).

If ϕ_i is the p-function of atom i, then the Coulomb integral is:

$$\alpha = \int \phi_i^* H \phi_i \, d\tau$$

and the resonance integral is:

$$\beta = \int \phi_i^* H \phi_{i\pm 1} \, d\tau$$

The molecular orbitals are then defined by:

$$\Psi_j = \sum_i c_{ji} \phi_i ; \quad j = 0, 1, 2, \ldots$$

and the bond order between atoms l and m is:

$$P_{lm} = \left| \sum_j n_j c_{jl} c_{jm} \right|$$

where the sum is over the occupied MO's labeled by j.

The charge density at atom i is:

$$q_i = \sum_j n_j (c_{ji})^2$$

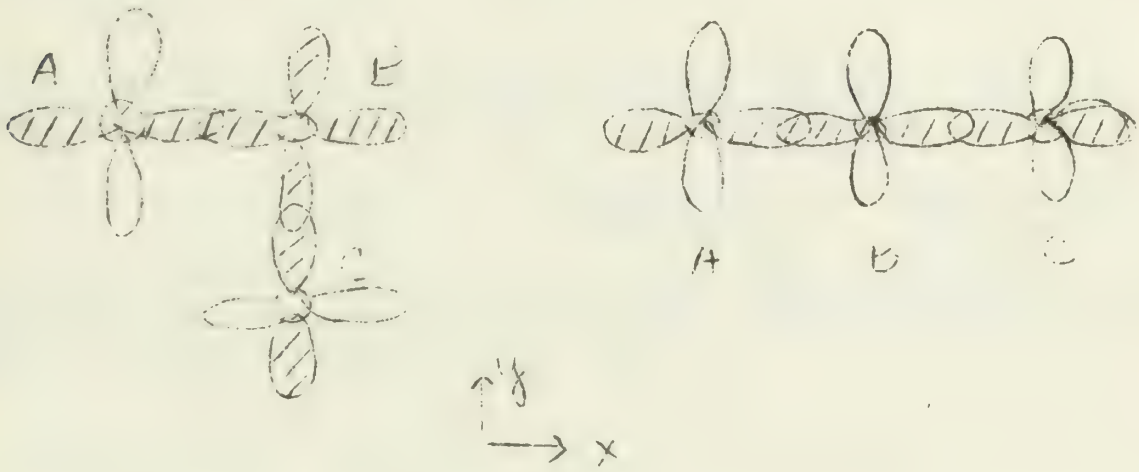
where n_j is the number of electrons in level j.

The calculations are made in two approximations: (a) as a zero approximation, all Coulomb integrals α are supposed to have the same value, regardless of the nature of the halogen atoms and their formal charges; (b) in a first

approximation, different Coulomb integrals are assigned to different atoms and to the same atoms with different formal charges: (i) For I, Br, Cl, and F the values α, $\alpha + 0.2\beta$, $\alpha + 0.4\beta$, and $\alpha + 1.0\beta$ are taken, respectively; the assumed differences in these values are approximately proportional to the differences in electronegativities of the atoms, with a proportionality constant of $2/3\beta$. (ii) A formal charge q, calculated for an atom in zero approximation, increases the absolute value of its Coulomb integral by $2/3\beta \times 0.3\,q = 0.2\,q\beta$. (This means that, following Pullman and Pullman (13), a charge q is taken to be equivalent to an increase of electronegativity of 0.3 q.) The first approximation is only applied when all bond orders in the part of the molecule being considered are equal to each other in zero approximation.

EXAMPLE: CALCULATIONS FOR $IBrCl^-$

The only configurations in which the p-functions overlap satisfactorily for any triatomic molecule are the rectangular and linear.



For the rectangular form, the functions which combine are the p_x-functions of atoms A and B and the p_y-functions of atoms B and C. This leads to twice the secular equation:

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0 \qquad \text{Solutions: } E = \alpha + \beta, \quad E = \alpha - \beta$$

There are 16 p electrons to be accommodated in the two MO's of energy $\alpha + \beta$, the two MO's of energy $\alpha - \beta$, and the five remaining atomic p-orbitals of energy α. One of the orbitals of energy $\alpha - \beta$ will remain empty, and the energy of the 16 electrons is $16\alpha + 2\beta$. Since this is the same as the

energy calculated for a halogen molecule and a halide ion separated from each other, no gain of energy is predicted for this angular negative trihalide ion.

For the linear form, the p_x-functions of atoms A, B, and C combine, leading to the secular equation:

$$\begin{vmatrix} \alpha - E & \beta & \beta \\ \beta & \alpha - E & 0 \\ 0 & \beta & \alpha - E \end{vmatrix} = 0 \qquad \text{Solutions: } \begin{aligned} E_1 &= \alpha - \beta\sqrt{2} \\ E_2 &= \alpha \\ E_3 &= \alpha + \beta\sqrt{2} \end{aligned}$$

The total energy of the 16 electrons is $16\alpha + 2\sqrt{2}\beta$, and a gain of energy of 0.83β is calculated compared with X_2 and X^-. Bond orders and atomic charges in zero approximation are:

$$\begin{array}{ccccc} & 0.71 & & 0.71 & \\ X & \text{———} & X & \text{———} & X \\ -0.50 & & 0 & & -0.50 \end{array}$$

The results in first approximation for the three possible linear configurations of the $IBrCl^-$ ion are:

$$\begin{array}{ccc} Br\text{—}I\text{—}Cl & I\text{—}Br\text{—}Cl & I\text{—}Cl\text{—}Br \\ 16\alpha + 5.04\beta & 16\alpha + 4.06\beta & 16\alpha + 4.87\beta \end{array}$$

The first configuration, which is actually observed, is calculated to have the lowest energy. Bond order and atomic charges in first approximation are:

$$\begin{array}{ccccc} & 0.75 & & 0.66 & \\ Br & \text{———} & I & \text{———} & Cl \\ -0.45 & & +0.07 & & -0.62 \end{array}$$

The most electronegative atom acquires the highest negative charge.

EXPERIMENTAL SUPPORT FOR MO DESCRIPTION OF BONDING

For the X_3^- ion, the MO's are represented in the following way in the zero approximation:

(anti-bonding) $\Psi_1 = \frac{1}{2}(p_A + p_C) + \frac{1}{\sqrt{2}} p_B$

(non-bonding) $\Psi_2 = \frac{1}{\sqrt{2}}(p_A + p_C)$

(bonding) $\Psi_3 = \frac{1}{2}(p_A + p_C) - \frac{1}{\sqrt{2}} p_B$

Of the 16 p electrons, 12 occupy the six p-orbitals not involved in bonding. Two are in the non-bonding orbital , which places electron density at atoms A and C. If the electronegativities of A, B, and C are the same, about half the electron density of the bonding orbital will belong to B, one quarter to each A and C, and half the non-bonding pair will belong to each of A and C. Since the non-bonding orbital puts extra negative charge on the terminal atoms, it can be correlated with the observation that the central atom of a trihalide is always less electronegative than the terminal atoms. Since only one bonding electron pair is used for the two bonds, this accounts in a natural way for the very considerable elongation of these bonds over the distance found in I_2 (14). Thus, the I-I bond distance in $\emptyset_4AsI_3$ is 2.90 Å., whereas twice the covalent radius of iodine is 2.68 Å.

The MO method predicts the correct bond angles, atomic configurations, and order of bond lengths for all polyhalogens except IF_7. These results are tabulated in reference 10. Only one more example, the I_5^- ion, will be listed here. The delocalization energies are given along with the configurations.

```
X — X — X        X — X — X        X        X — X — X — X — X
         X               X      X — X — X          1.46 β
1.66 β   X               X               X — X — X — X
                         X                        X
                  1.66 β        1.66 β        1.23 β
```

```
I — I — I        I — I — I        I
         I               I      I — I — I
1.76 β   I               I  1.67 β        1.49 β
```

In zero approximation, three models are energetically equivalent, but in first approximation the configuration actually observed in $N(CH_3)_4I_5$ (9) has the lowest energy.

```
      0.73     0.68                  2.93     3.14
I ———— I ———— I                 I ———— I ———— I
                 0.68                            3.14
                 I                               I
                 0.73                            2.93
                 I                               I
```

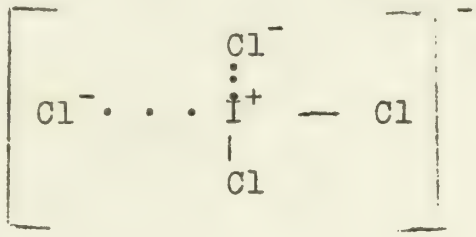
Calculated bond orders Observed bond lengths

The nuclear quadrupole coupling constants have been measured by Cornwell and Yamasaki for both Cl^{35} (15) and

I^{127} (16) in alkali salts of ICl_2^- and ICl_4^-. The results can be most easily interpreted by translating the MO description of these ions into their equivalent description in terms of resonating valence bond structures.

ICl_2^- : $^-Cl \cdots I - Cl \leftrightarrow Cl - I \cdots Cl^-$

ICl_4^- :



The value of the coupling constant, eQq/h, for Cl^{35} in ICl_2^- and in ICl_4^- is about half of that found in ICl. The I^{127} values are roughly the same in all three species. The conclusions based on these results are that the I-Cl bonds in the two ions have a rather large proportion of ionic character, corresponding to the presence of a net negative charge of roughly half an electron on each Cl atom. Since hybridization involving promotion from the 5p to the 5d, or possibly 6s, level would raise the iodine resonance frequencies markedly from the value found in ICl, the attainment by iodine of higher valencies in these ions is due more to transfer of charge to chlorine atoms than to promotion to higher orbitals of iodine. These results substantiate the MO description of bonding and show conclusively that d orbitals cannot be included in the bonding scheme to the extent required by the spd hybridization model. These same results were obtained independently by Japanese workers who also measured the Cl^{35} resonances in these ions. The estimated ionic nature of the I-Cl bond in ICl_2^- was 66%; and in ICl_4^-, it was 59%. The values they calculated by the MO method were 61% and 57%, respectively, in good agreement with observations (17).

The infrared and Raman spectra of ICl_2^-, ICl_4^-, $BrCl_2^-$, and Br_3^- have been obtained and the stretching force constants calculated (18). The values of f_r, the stretching force constant, for the trihalide ions are roughly half the values for the free halogens, and the values of the interaction force constants f_{rr} between bond stretching coordinates at an angle of 180° to each other are very large (approximately 35% of the value of f_r). These rather unusual force constants have been interpreted in terms of bonding using p orbitals. The similarity between these force constants and those for HF_2^- are pointed out.

Table I. Bond Stretching Constants for Some Polyhalogen Ions and Molecules.

Ion	f_r(md/A)	f_{rr}(md/A)	$f_{rr'}$(md/A)	$\frac{f_r(xyx)}{f_r(xy)}$	f_{rr}/f_r
ICl_2^-	1.00	0.36		0.46	0.36
ICl_4^-	1.25	0.33	0.08	0.53	0.26
ICl	2.38				
$BrCl_2^-$	1.29	0.26		0.47	0.20
BrCl	2.83				
Br_3^-	0.91	0.32		0.38	0.36
Br_2	2.45				
HF_2^-	2.31	1.72		0.23	0.72
HF	10				
CO_2	15.5	1.3		0.82	0.08
CO	19.0				

An MO treatment in terms of chains of I_3^- has been applied successfully to explain the metallic nature of the starch-iodine complex, including the measured weak paramagnetism and electronic conductivity (19). In terms of the MO theory, a row of iodine atoms (50 to 500) behaves as a one-dimensional metal with a band of energy levels to accommodate the 5p-electrons of the I_3^- chain. The optical absorption properties are also consistent with the metallic model. The 6250 Å absorption may be ascribed to a transition to the σ band from a π band. The model predicts, and thus explains, the electron spin resonance of the complex in the right order of magnitude (about 10^{15} unpaired electrons per gram).

Bersohn (20) has employed delocalized molecular orbitals to explain intermolecular bonding in solid iodine. The band structure of solid iodine is worked out on the assumption that electron exchange between layers of iodine atoms is negligible and that only p-functions are used by the iodine atoms. Just as the halogen molecule is formally analogous to ethylene in MO description, so is the solid halogen to graphite. Each halogen atom is assumed to interact with three neighboring atoms in the plane. The model is justified

by its simple description of the iodine nuclear quadrupole coupling constant, the anisotropy of the electrical conductivity, and the optical absorption.

The MO calculations can be used in a qualitative way to explain some thermodynamic properties of the polyhalogens. Qualitative agreement between theory and experiment is obtained when the energies of formation calculated in first approximation for simple interhalogens are compared with experimental values. (ΔH^{+} refers to the formation of gaseous XY from gaseous X_2 and Y_2 at 25°C. and 1 atm. pressure.)

Table II. Calculated and Observed Heats of Formation (11)

Compound	ΔE (calc.)	ΔH^{+} (obs.) kcal/mole
IF	0.24 β	-30.1
BrF	0.15 β	-18.4
ClF	0.09 β	-13.4
ICl	0.04 β	- 3.35
IBr	0.01 β	- 1.42
BrCl	0.01 β	- 0.21

Compounds containing $BrICl^-$ ion decompose into a monochloride and BrI. This is partially ascribed to the high lattice energy of the crystalline monochloride formed, as compared with the energy of the corresponding bromide or iodide. The reaction energy ΔE as calculated by the MO method for the three possible decompositions of the free $BrICl^-$ ion is:

$$BrICl^- \rightarrow Cl^- + BrI \qquad \Delta E = -0.82\ \beta$$

$$BrICl^- \rightarrow Br^- + ICl \qquad \Delta E = -1.00\ \beta$$

$$BrICl^- \rightarrow I^- + BrCl \qquad \Delta E = -1.22\ \beta$$

The fact that the calculated dissociation energy is smallest for the first reaction may be an additional explanation for the experimentally observed method of dissociation (11).

The existence of the xenon fluorides XeF_2, XeF_4, and XeF_6 also supports the validity of the MO description of bonding in the polyhalogens. The compounds XeF_2 and XeF_4 are isoelectronic with ICl_2^- and ICl_4^-, respectively. In fact,

Pimentel (8) predicted in 1951 that a rare gas could form complexes with halogens on the basis of his MO treatment of the polyhalogens. The compound XeF_2 is linear (21), and XeF_4 is square planar, with the average distance between Xe and F being 1.92 Å. (22) Rundle (23) argues that because of the especially high promotional energies of the rare gases, the bonding in XeF_2 and XeF_4 has little possibility of using outer d-orbitals; so the existence of these xenon fluorides in itself is evidence in favor of delocalized bonds using only p-orbitals of the valence shell.

Smith has observed the infrared spectrum of XeF_2 and has interpreted the results to show that the bond length is too short and the interaction force constant too small for an explanation of the bonding in terms of p orbitals (21). However, Pimentel and Spratley (24) argue that the IR data can be reasonably interpreted in terms of an MO bonding description, since the molecules XeF_2 and ICl_2 involve quite different formal charge distributions. In XeF_2, the xenon atom must have a significant positive formal charge to balance the negative charge placed on the terminal atoms, whereas the iodine atom has a formal charge close to zero. This difference can be expected to strengthen the Xe-F bond because of the electrostatic attractions. At the same time, the interaction force constant should be reduced, because an asymmetric displacement is no longer favored energetically over a symmetric displacement. In the symmetric mode, the terminal atom repulsions that tend to raise the energy are counteracted by the central atom positive charge.

CONCLUSION

There is a considerable amount of evidence, both structural evidence and that based on other physical methods which give information concerning bonding in molecules, that a molecular-orbital description involving delocalized bonds formed from atomic p-orbitals is a much closer approximation to the true bonding in polyhalogen species than the description using outer d-orbitals in an spd hybrid model.

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